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TABLE III

Illustrative Silicone Resin Compositions

| EXAMPLE | STARTING | MIXTURE RATIO OF | | SUBSTITUTED | | OTHER ADDITIVES | |
|---------|--------------------|-------------------------|------------|--------------|--------------------------------|-----------------|--|
| | | PACKAGED | | BENZOPHENONE | | | |
| NO. | SILICONE RESIN | COMPONENTS ¹ | NAME | PARTS | NAME | PARTS | |
| 1 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | 7127 Accelerator | 5/10 | |
| 2 | Silastic® 595 LSR | 1:1 | Uvinul 400 | 5 | Syl-Off® 17611 ⁽²⁾ | 50 | |
| 3 | SLR 5100 | 10:1 | Uvinul 400 | 5 | Sylox® 2 ⁽³⁾ | 8 | |
| | Liquid BC-10 | 1:1 | | | | | |
| 4 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | Hydriol® 710 ⁽⁴⁾ | 10 | |
| 5 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | Silopren® LSR | 1 | |
| | | | | | Z3042 ⁽⁵⁾ | | |
| 6 | SLR 5500 | 10:1 | Uvinul 400 | 5 | | | |
| 7 | Silopren® LSR 2540 | 1:1 | Uvinul 400 | 5 | | | |
| 8 | SLR 5300 | 10:1 | Uvinul 400 | 5 | | | |
| 9 | SLR 5106 | 10:1 | Uvinul 400 | 5 | | | |
| 10 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | Fluorag Agent | 4 | |
| | | | | | OK412 ⁽⁶⁾ | | |
| 11 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | Nalco® 1SJ-612 | 50 | |
| | | | | | Colloidal | | |
| | | | | | Silica ⁽⁷⁾ | | |
| 12 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | Nalco® 1SJ-614 | | |
| | | | | | Colloidal | | |
| | | | | | Alumina ⁽⁸⁾ | | |
| | | | | | 250 Fluid ⁽⁹⁾ | 7 | |
| 13 | Silastic® 595 LSR | 1:1 | Uvinul 400 | 5 | | | |
| 14 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | | | |
| 15 | Silastic® 595 LSR | 1:1 | Uvinul 400 | 5 | Zepel® 7040 ⁽¹⁰⁾ | 3 | |
| 16 | Silastic® 595 LSR | 1:1 | Uvinul 400 | 5 | Zonyl® UR ⁽¹¹⁾ | 1/10 | |
| 17 | Silastic® 595 LSR | 1:1 | Uvinul 400 | 5 | Zonyl® FSN-100 ⁽¹²⁾ | 1/10 | |
| 18 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | DLX-600 ⁽¹³⁾ | 5 | |
| 19 | Silopren® LSR 2530 | 1:1 | Uvinul 400 | 5 | TE-3608 ⁽¹⁴⁾ | 5 | |

Table II Footnotes:

⁽¹⁾Ratio listed is that recommended by the manufacturer.⁽²⁾Syl-Off® (registered trademark of Dow Corning) is a crosslinker.⁽³⁾Sylox® 2 (registered trademark of W. R. Grace Co.) is a synthetic amorphous silicon.⁽⁴⁾Hydriol® 710 (registered trademark of Alcoa) is hydriated aluminum oxide.⁽⁵⁾Silopren® LSR Z3042 (registered trademark of Mobay) is a silicone primer (bonding agent) mixture.⁽⁶⁾Fluorag Agent OK412® (registered trademark of Degussa Corp.) is a wax coated silica dioxide.⁽⁷⁾Nalco® 1SJ-612 Colloid of Silica (registered trademark of Nalco Chemical Company) is an aqueous solution of silica and alumina.⁽⁸⁾Nalco® 1SJ-614 Colloid of Alumina (registered trademark of Nalco Chemical Company) is an aqueous colloidal alumina dispersion.⁽⁹⁾250 Fluid (registered trademark of Dow Corning) is a 100 centistoke viscosity dimethylpolysiloxane.⁽¹⁰⁾Zepel® 7040 (registered trademark of duPont) is a monosonic fluoropolymer.⁽¹¹⁾Zonyl® UR (registered trademark of duPont) is a monosonic fluorosurfactant.⁽¹²⁾Zonyl® FSN-100 (registered trademark of duPont) is a monosonic fluorosurfactant.⁽¹³⁾DLX-6000® (registered trademark of duPont) is polytetrafluoroethylene micropowder.⁽¹⁴⁾TE-3608® (registered trademark of duPont) is a polytetrafluoroethylene micropowder.

Example 20

Internally Coated Fiber Encapsulated, Interstice Filled Fabric Preparation

A complete, stepwise, application of the inventive method in the production of an encapsulated fiber fabric was as follows:

The selected base fabric was TACTEL® (gold color) #612071 available from ICI Americas, Inc. This fabric was 100% woven nylon. If desired, this and other fabrics may be calcendered to modify surface texture, geometry and porosity. The fabric was weighed and measured. Its initial weight is 3.1 ounces per square yard. Its thickness equals 9 mils. The fabric was next washed with detergent, rinsed thoroughly, and hung to air dry. The fabric was soaked in water, wrung dry, and weighed. The water retained was equal to 0.8 g water/g fabric. The fabric was then treated with a water repellent fluorochemical, a 2% solution by weight of Zepel® 7040. In order to do so the fabric must be soaked in a 2.5% solution of Zepel® water-repellent chemical in distilled water. This was because:

$$\frac{1 \text{ g fabric} \cdot (0.02)}{0.8 \text{ g water}} = 0.025$$

The treated fabric was then run through a wringer and air dried. Next, the fabric was heated in an oven for 1 minute at 350°. This heating sinters the water repellent fluorochemical. The fabric with its fluorochemical residue is then run as in the FIG. 7 embodiment. The silicone polymer composition is applied at 1.0 oz./sq. yd. The polymer composition is GE 5108 A/R in a 1:1 ratio and can be considered to be a viscoelastic liquid that flows only under the shear forces resulting from the pressured controlled placement. The polymer composition is believed to return very substantially to its original viscous condition almost immediately upon release of the pressure. The polymer composition was believed to flow a short distance within the matrix of the fabric during the short time that it was, because of pressure shearing forces, of lowered viscosity. Therefore, a number of "flows" may be usefully generated with multiple blades in order to properly distribute the polymer composition in its preferred position substantially encapsulating the surfaces of the fabric's fibers.

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Finally, the treated fabric was run through a line oven, of approximately 10 yards in length, at 4-6 yards per minute, and was cured at 325°-350° F. It then passed through a series of idler rollers and is rolled up on a take-up roll, completing the tension zone. The resultant fabric has a non-tacky thin film of silicone that was internally coated to form a fiber encapsulated, interface-filled layer in the fabric.

Example 21

Evaluation of Fiber Encapsulated Fabric Properties

The test results of the original versus the produced fiber encapsulated fabric of Example 20 were as follows:

TABLE IV

| FABRIC | ORIGINAL FABRIC | ENCAPSULATED |
|-----------------------------------|-----------------|---------------------|
| Spray Rating (1) | 20 | 100 (reverse = 100) |
| Rain Test (2) | Fail | Pass |
| Abrasion Test (cycles) (3) | 1,200 | 3,200 |
| Molauere Penetration (4) | Saturated | 0.8 g |
| Hydrostatic Resistance (psi) (5) | 1 | 2 |
| MVTR (g/m ² /day)* (6) | 4,434 | 2,362 |
| Weight (oz/yd ²) | 3.1 | 4.1 |

Amount Impregnated = 1.4 oz/yd²

*Environmental chamber at 104° F and 74% humidity

TABLE V

| LAUNDERING TEST | TIMES WASHED | | | |
|------------------------------|--------------|----|-----|-----|
| | Initial | 5m | 10m | 15m |
| (Spray Rating) | | | | |
| Impregnated Side | 100 | 90 | 90 | 90 |
| Reverse Side | 100 | 90 | 90 | 90 |
| Unimpregnated Treated Fabric | 100 | 90 | 90 | 40 |

Accelerated Weathering Test (8)

Samples placed in QUV weatherometer for 72 hours.

Original=7

Impregnated Side=9

Reverse Side=8

- (1) The spray test was conducted in accordance with AATCC 22-1974. It measures water repellency of a fabric sample on a scale of 0-100, with a reading of 100 designating a completely water repellent fabric.
- (2) The rain test was conducted in accordance with AATCC 35-1985. It measures resistance of a fabric sample to penetration of water under static pressure from a shower head of 3 feet/5 minutes. A fabric is stormproof when less than 1.0 gram of water is absorbed by a standardized blotter used in the test.
- (3) The abrasion test was conducted in accordance with Federal Test Method Standard 191 A, Method 5306. Abrasion resistance is measured by mounting a fabric sample on a Taber Abraser Model 174 and measuring the number of cycles before the fabric begins tearing apart.
- (4) The hydrostatic resistance test was conducted in accord with Federal Test Method Standard 191A, Method 5512. The test measures a fabric samples' resistance to water under pressure using the Mullen's Burst Test methods and apparatus. Test results are expressed in pounds per square inch at which water beads penetrate the fabric.
- (5) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104° F and 47% humidity.

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(6) A laundering test of the conventional household type was performed. Fabric samples were washed with Tide® detergent. There was no drying. A spray test was subsequently carried out after each wash to determine the effect of the washing.

(7) The accelerated weathering test was conducted in accordance with ASTM G-53. Samples of original and impregnated fabrics were placed in the weatherometer of QUV Company and results were compared (All readings were based on a graduated color scale of 0-20, 10 designated the original color, while 0 designated a white out.)

Example 22

Iodine As A Biocidal And Antimicrobial Agent with Polyurethane as a Reactive Site

This example demonstrates the preparation of a biocidal or self-sterilizing web. Polyurethane, Sanocon® 898 in a latex form, was mixed with silicone polymer, Dow Corning 2962 (Parts A & B 50:50) in the ratios of 0%, 5%, 10%, 15% and 100%, by weight respectively. Various fabric webs such as Burlington 4040, 4045 and Versatec, were treated with 15-20% weight add-on of the above polymer mixtures in accordance with the practice of this invention. The fabrics were cured at 350° F (176° C.) for 26 seconds. The treated fabrics were dipped in an iodine solution bath containing 2% iodine in a 2.4% KI solution or 2% iodine in an ethanol solution for 10-30 seconds at room temperature and rinsed in a freshly-distilled water bath until no free iodine came off. The iodine/silicone/urethane-treated fabrics were then air dried and observed to be yellowish on the silicone/urethane treated side, indicating the presence of iodine.

A culture of XL Blue *E. Coli* was prepared in a refrigerated LB Agar and grown for 9 hours. Two drops of cultured XL Blue *E. Coli* were added to four streaked LB Agar plates and spread with a bent sterile 1 mL pipette. The iodine/silicone/urethane-treated fabric web samples were placed (treated side down) on the LB Agar plates and grown in an incubator at 37° C. After 24 hours, an area of growth inhibition was observed for all samples, which is indicative of the active killing sites for each piece of treated fabric. The treated fabric was then washed, charged with free iodine and then re-tested for antimicrobial activity. The growth of bacteria was inhibited both under and around the treated fabric samples.

A latex web, instead of a fabric web, when treated with silicone/polyurethane, also shows the ability to bind free iodine. After dipping in 2% iodine ethanol solution, the iodine/silicone/urethane-treated latex web samples were placed on LB Agar plates. Again, bacteria growth inhibition was observed both under and around the samples.

Example 23

Protein Additives As Hand Altering Agents, Surface Chemistry Modifiers And Antibody Binding Sites

The proteins used in the practice of this invention were "Silk-Like-Protein 3 (SLP-3)," produced by Protein Polymers, Inc. (San Diego, Calif.) and "Crosilk," produced by Cnda, Inc. (New York, N.Y.). Crosilk is a 10,000 molecular weight protein made by hydrolyzing silk, and is comprised of 17 different amino acid segments, ranging in percent weight of 0.1% to 20.3%. The silicones used herein are Mobay Silopren® LSP 2530 and Dow Corning Silastic® LSR 2303. The webs used herein are Eggplant Supplex, Black Cordura, and a 48% Nylon/52% Cotton blend.

Prior to mixing the protein with the silicone polymer, the dimensions of the protein particles need to be adjusted to a suitable particle size such as 0-2 microns in length and 0-2 microns in diameter. This can be accomplished by grinding

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the protein particles with a small amount of silicone polymer, in a ball mill in a solvent such as xylene. The solvent is used to lower the viscosity of the silicone polymer composition in the ball mill.

Generally, the mixture in the ball mill is composed of about 5% SLP-3, 50% silicone polymer composition and about 45% of xylene. The grinding of protein can also be done without a solvent. After grinding, additional silicone polymer composition was added to the protein/silicone mixture to produce a mixture containing about 2.5% by weight protein. The xylene solvent evaporates during this process. The final protein/silicone mixture was then applied to the webs in accordance with the practice of this invention. The treated web was cured at 320° F. for 2 minutes. Any xylene residue remaining evaporates during the final curing stage. The resulting webs showed improved hand feel (softness), moisture vapor permeability, and surface exposure as shown by further binding tests with antibodies. The permeability test results are summarized in the following table.

TABLE VI

MVTR Results of Webs Treated with SLP-3 Protein Additive

| Materials | MVTR (g/m ² day) | Permeability |
|----------------------|-----------------------------|--------------|
| Eggshell | 464 | — |
| ISP2530 w/SLP-3 | 1504 | 156% |
| Eggshell + DWR | 2089 | — |
| ISP 1530 w/SLP-3 | 2718 | 130% |
| Black Carlin | 3387 | — |
| ISP 2303 w/SLP-3 | 4115 | 122% |
| Black Carlin | 2023 | — |
| ISP 2530 w/SLP-3 | 9799 | 347% |
| 40% Nylon/50% Cotton | 4076 | — |
| ISP 2530 w/1% SLP-3 | 4203 | 103% |
| ISP 2530 w/5% SLP-3 | 4203 | 103% |

DWR — Durable Water Repellent such as a Fluorocarbon composition.

Each row shows both the control sample (without polymer and without SLP-3 protein) and a treated web sample with the polymer and the SLP-3 protein additive. The moisture vapor transport rate increased with the SLP-3 protein. This shows that the protein assists in the transport of moisture vapor. Samples of webs treated with the SLP-3 protein additive were exposed to the SLP-3 antibody, washed, then exposed to radioactively labeled "protein A," washed, and then analyzed for the radioactively labeled "protein A." Protein A is a bacterial protein which has specificity for antibodies. The tested samples contained 1% and 5% by weight SLP-3 protein and then antibodies were attached. The control samples contained the same amount of SLP-3 protein but no antibodies. The result was that the samples containing more SLP-3 protein showed larger amounts of antibodies. This result shows that the SLP-3 protein was surface exposed and created a binding site for antibodies.

Crosslink was used as an additive in Mohay ISP 1530 silicone polymer. This mixture was applied to webs such as Arthur Kahn Blue Cotton, Arthur Kahn White Tactel and Patagonia Red Supplex. All webs were cured two minutes in an oven at 320° F. The presence of the hydrolyzed silk did not inhibit the cure of the silicone polymer. The treated webs showed a slightly improved feel and no real appreciable difference in the MVTR results of the fabric. This result shows that although various proteins can be utilized, the same functionality does not appear. Some proteins can be used specifically for binding antibodies, some for altering the "feel" of the fabric, some for modifying the surface characteristics of the polymer and/or web, and some for altering the moisture vapor transport rate.

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Example 24

Pigments, Dyes and Proteins on Fibers

This example illustrates the addition of pigments, dyes, and proteins to polymers and the application of the polymer compositions onto fibers. The following is a preferred procedure for processing fibers, particularly for use in carpets.

1. Tension a single bundle of fibers across a lab encapsulator. This set-up presents a knife-over-air process condition on the carpet fiber.
2. Comb the fibers using a very fine comb to individually isolate the filaments to prevent them from sticking or spot welding together.
3. Apply the polymer composition with the dye, pigment, or protein mixed into it, onto the surface of the tensioned fibers.
4. Take semi-dull encapsulating applicator, such as a flex knife, and shear the polymer composition to get a uniform, fully encapsulated fabric.
5. Once again, comb fibers to individually separate and prevent them from sticking together.
6. Pin the comb to one end of the lab encapsulating frame and cure the polymer composition.

The above process was used to apply a red pigment onto Nylon 6 CF carpet fibers. The polymer composition used was a 50/50 DG2303 mixed with A-50 red pigment. Twenty lbs. of tension was applied across the fibers. The flex knife was pulled across the fibers ten times to shear thin the polymer composition. The treated fibers were cured for five minutes at 320° F. The red pigment appeared uniformly around the fibers when examined under a microscope.

The above process was also used to apply a polymer composition and a red pigment onto BASF 70/32 Bright Tri-Lobal Nylon 6 yarn. Seven 14 inch strands were tensioned at about 10 lbs. The polymer composition was SLC 5106 A&B in a 10:1 ratio mixed with 30% weight add-on of silicone red (8010.94 40% pyrazalene-VT). The composition was shear thinned and then cured at 320° F. for five minutes. The red pigment appeared uniformly around the fibers when examined under a microscope. This shows the encapsulating aspect of the polymer composition and the ability to introduce red dyes and pigments around individual fibers.

The above process was also used to apply the SLP-3 Beta silk protein to individual fibers. The polymer composition used was DC-2303 A&B in a 1:1 ratio mixed with 10% by weight of SLP-3 Beta silk protein. The protein was ground up in a mill grinder before addition in the polymer composition. Ten lbs. of tension was applied. The fibers were washed with warm water and then dried. Six shears were applied with the shearing means on the top and bottom of the fibers. Between shears, the excess was wiped off. The composition was cured at 320° F. for five minutes. The presence of the SLP-3 protein was seen uniformly around the fibers under a microscope.

Additional samples were run using the same procedure, and the results are shown in the table below:

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TABLE VII

| Company | Product Description | Obstacles | Solution | Process | Successes |
|-----------------|--|---|--|--|--|
| Shaw Industries | 1800 Denier Bulk Polypropylene Beige | Sensitive to heat | Add platinum Reduced cure heat | Heat set 5/5 shear Appears to be encapsulated | Addition of Red Dye in polymer Ran SLC \$106 Tried platinum accelerator |
| Shaw Industries | 2600 Denier Dull Polypropylene Blue | Sensitive to heat Colored Fiber | Add platinum Reduce cure Use DC303 | Heat Set Reduce heat cure Appears to be encapsulated | Addition of Red Dye Ran SLC \$106 Success with accelerator Appears to encapsulate |
| Shaw Industries | 3040 Denier Nylon 6 Fiber Bulk Multicolor | Multiple Fibers Fiber Welding Bulked Tri-Lobal Fiber | Use all polymers High shear Cure related High speed shear | Heat set 5/5 shear Add accelerators Appears to be encapsulated | Reduces shrinking Tried all polymers Isolated heat process 35 mm picture taken Tried acrylic acrylic Tried SLC\$106 |
| BASF Corp. | M/32 Brl Tri-Lobal Nylon 6 for Textiles | Small Filament Tightly spun Residual Tri-Lobal | High tension High shear Water clean High speed | Appears to be encapsulated b/s shear Appears to be encapsulated | Tried Red Dye in polymer |
| BASF Corp. | Nylon 6 Unbulk 8800 Denier CF Yarn White | 8800 Denier Fiber Welding Residuals | Alt. Process Splitting up fiber Water wash Solvent wash | 6/6 shear Appears to encapsulate Tried all polymer Curing process | Tried all polymers Red Dye in polymer Picture taken Added encapsulation Trying to process all fiber |
| DuPont | Astoria Nylon Bulk Fiber | Bulked Faceted Fiber Residuals Fiber Welding | High Tension High shear 6/6 shear Heat set Cure relax zone | Heat set 6/6 shear Appears to encapsulate Add Red Dye Cure related | Red Dye in polymer Tried SLC\$106 Add accelerators Need better flow character Try different polymer |
| DuPont | Bulked Twisted Flatbed Astoria Carpet Yarn | Thick Yarn Mulu-Tuak Residuals Etching/chemical | High Tension High speed High shear Alt. polymer | 10/10 shear Shear blade Add accelerator Tried SLC\$106 Red Dye | Shear thinning Increased bulk Fiber welding Higher speed needed |

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Example 25

A Flattening Agent as an Additive

In this example, the look of the treat web was flattened by adding an amorphous silica compound labeled OK 412, produced by Degussa, Inc. (Frankfurt, Germany), available through its pigment division in Teterboro, N.J., to the silicone polymer prior to application the web. The introduction of this material into the silicone polymer reduced the glossy look of the final cured silicone composition, allowing the web to maintain its cotton-like look and hand. The silicone polymer used herein is Mobay Silopren® LSR 2530. The flattening agent OK 412 was mixed in the ratio of 80% by weight LSR 2530 A/B, 17% by weight OK 412, and 3% by weight White mineral spirits. The mixture was then applied in accordance with the practice of this invention, to Milliken Poplin (65% polyester/35% cotton) and Arthur Kahn Dune (100% cotton), respectively. The webs were pre-treated with a 3.5% fluorochemical solution of F31X durable water repellent (DWR). The silicone/OK 412 treated webs were cured in an oven at 350° F. for 1.5 minutes. All webs treated with the silicone/OK 412 mixture showed significant improvement in abrasion resistance while flattening the glossy look and maintaining the feel of the web. The test results of the above samples are summarized in the following table:

TABLE VIII

Test Results of OK 412 Treated Webs

| 40 Fabric Materials | Spray Test | Rain Test | Abrasion Test |
|--|------------|-----------|---------------|
| Milliken Poplin (65% polyester/35% cotton) | 0 | untreated | 75 cycles |
| LSR 2530 w/OK412 + DWR | 00 | 0 g | 125 cycles |
| Arthur Kahn Dune (100% cotton) | 0 | untreated | 75 cycles |
| LSR 2530 w/OK412 + DWR | 90 | 0 g | 150 cycles |

DWR — Durable Water Repellent such as a fluorocarbon composition.

Each row shows both the control sample (without polymer and without additives) and a treated web sample with the polymer and the OK 412 additive.

Example 26

Topical Application of a Flattening Agent

In this example, the look of the treat web was flattened by topically applying an amorphous silica compound labeled OK 412, produced by Degussa, Inc. (Frankfurt, Germany), available through its pigment division in Teterboro, N.J., to the silicone polymer treated web prior to curing. The introduction of this material upon the silicone polymer treated fabric reduced the glossy look and altered the feel of the fabric after curing. The silicone polymer used herein is GE 6108 A/B (1:1).

The fabric was a Navy Blue 3-ply Supplex (100% Nylon). The fabric was stretched to a tension of 15 Newtons. The polymer was applied and shear thinned into the fabric using a shearing knife. The polymer weight add-on was approximately 29%. The samples were then sprinkled with OK412. This was done with a fine screen that dispersed the powder

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upon staking. The sample was then passed under a nip to force the additive into the fabric and into the polymer composition. The sample was cured for 30 seconds at 350° F. A sutter test was run on the sample and the sample was rinsed with water and dried.

Upon rinsing the fabric the white spots on the navy blue supplex disappeared. After drying, the spots reappeared, indicating that the additive adhered to the polymer composition in the fabric. This shows that a topically applied additive will adhere to the polymer composition and will retain its functionality.

Example 27

Copper Particles as an Additive

This example demonstrates the preparation of a web containing sub micron copper particles. Sub micron copper particles were mixed with silicone polymer, Dow Corning 2303 (Parts A&B 50:50) in the ratios of 0%, 5%, 10%, and 20% by weight respectively. Various fabric webs such as Burlington 4040, 4045 and Veratec, were treated with 15-20% weight add-on of the above polymer mixtures in accordance with the practice of this invention. The fabrics were cured at 350° F. (176° C.) for 26 seconds. The samples were then examined with scattering electron microscopy (SEM). The results appear in FIG. 6f and are discussed in the following examples explaining the SEM figures.

Example 28

Description of Fabric Controlled Placement Through Scanning Electron Microscope (SEM) Photomicrographs

FIG. 6a depicts a cut end of a filament illustrating a thin film encapsulation in white. A crack was created in the filament with a high temperature electron beam. This crack continues under the surface of the thin film. The filament has been cut and the thin film has been stretched or elasticized by the cutting of the filament. The two arrows in the upper right corner show the thickness or distance represented by the black box in the lower right corner as 126 nm.

FIG. 6b depicts an isolated image on 330 Denier Cordura single filament fiber processed with the micro-finish fiber coating technology, magnified 5,720 times. The Bioengineered Comfort™ polymer containing engineered protein and solid silicone was used in the process with a moderate degree of shear. The image on top of the fiber is an undispensed protein polymer which clearly illustrates the presence of the protein after the micro-finish fiber coating process. The surface morphology has very small protein polymer particles encapsulated in the solid silicone polymer and is homogeneously dispersed throughout the film system on the fiber.

FIG. 6c is an image of a white nylon magnified 178 times. The application side is shown at the bottom left hand corner of the image. The upper portion of the image is the non-application side. At the upper right corner is the intersection of the warp and fill fiber bundles, where the polymer presence can clearly be seen on the fibers. The internal layer of polymer that creates the liquid barrier or resistant property can be seen along the bottom right corner of the picture. This internal layer is a combination of polymer filling some interstitial spaces and polymer "glueing" together the fibers and filaments of the web.

FIG. 6d depicts the surface of a circular fiber that has had a defocused broad electron beam of approximately 2000 degree centigrade defocused across the image area. The imaging shows a destructive burn pattern of a fluorochemical package on the surface of the silicone film. On the surface of the filament the image depicts the surface migration of the fluorochemical from the fiber through the thin film and oriented on the surface of the silicone

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FIG. 6e is a Tunneling Electron Microscopy (TEM) image of a thin cross section of a filament encapsulated with polymer. The lighter image on the lower side of the frame is a polyester filament. The black spherical dots on the outer edge of the fiber are extremely dense processed material. In this imaging technique, the darker the image, the denser that specific material.

FIG. 6f depicts a nylon fabric magnified 419 times with bright particle tracer images and a cross sectional image of a nylon fabric. These bright particles are submicron metal particles dispersed throughout the fabric in the processed film. The addition of bright copper submicron particles in the polymer allows secondary back scatter mode to illustrate the complete encapsulation ability of the controlled placement technology. The left side of the image is the performance side of the fabric which is the non-application side of the polymer, but it is clear, with the presence of the glowing brightness of the copper submicron particles throughout the performance side of the fabric, that controlled placement technology successfully encapsulates completely around the fibers throughout the fabric structure. The other clear unique feature of the controlled placement technology is that each fiber is still independent. This differentiation allows the controlled placement technology's processed fabrics to retain exceptional hand and tactile quality, while still imparting performance characteristics. On the left side of the fabric, directly underneath the printed text "performance side", an elemental analysis was conducted and the outcome of that analysis is depicted in FIG. 6g. The result clearly shows a strong presence of submicron copper particles.

In the next examples that involve accelerated weathering, abrasion, water repellency, moisture penetration, and rain testing, data is provided for a Tactel fabric identified as Deva Blue. The fabric is 100% nylon, available from Arthur Kahn and identical in composition, preparation, and enveloping specification to that of the Hot Coral presented in previous examples.

Example 29

Accelerated Weathering Test

The results of weathering upon a treated web of this invention are shown in actual tested sample pieces comparing original fabrics with embodiments of the enveloped fiber fabrics of this invention.

In every case, the enveloped fiber fabric samples were found to have significantly better weathering characteristics than the original untreated fabrics as determined by accelerated weathering tests. Even the reverse side (compared to the treated side) of an enveloped fiber nylon fabric of the Tactel® type was improved over the original fabric. In addition, the excellent "hand" of the enveloped fiber fabric was found to have been maintained after the accelerated weathering test.

The test performed conforms to each of the following performance standards:

- ASTM G-53 light/water exposure materials
- ASTM D-4329 light/water exposure-plastics
- General Motors Test spec TM-58-10
- ISO 4892 Plastics exposure to lab light

The procedure used for the accelerated weathering testing involved subjecting fabric samples to four hours of high-intensity ultraviolet light, alternating continuously with four hours of water condensation, wetting the fabric in the dark. This alternating exposure (four hours on, four hours off) to high-intensity ultraviolet light and water wetting, simulates outdoor environmental conditions in a vastly accelerated manner, quickly degrading unprotected dyes and fibers. The

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methods and apparatus used for this test was a QUV Accelerated Weathering Tester from The Q-PANEL Company, 26200 First Street, Cleveland, Ohio 44145.

The results obtained on some sample fabrics are expressed in Table VII. In this Table, results are expressed in the form of "A/B" where A and B are numbers. The number "A" is the color rating on a graduated scale from 0 to 10. The number 10 equals perfect (original) condition where 0 equals a white color and a completely faded fabric. The number "B" is the number of hours of weathering transpiring when the number "A" rating was obtained.

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original (untreated) fabric specimen. The procedure used was as follows:

1. A test specimen of the fiber enveloped fabric with a 7 inch diameter was cut.
2. An equally-sized specimen of control (untreated) fabric was cut.
3. The fabric specimen was mounted on the rotating wheel securely and the clamps were screwed down.
4. The counter was set.
5. The vacuum power adjustment was set. (For this experiment, vacuum was set at 80.)

TABLE IX

| Accelerated Weathering Testing | | | | COLOR RATING (RATING/HOURS) 10 = PERFECT 0 = WHITE COLOR FADES OUT |
|---|------------------------------|----------------------------------|------------------------------|---|
| ORIGINAL FABRIC | ORIGINAL FABRIC WEATHERED | ENVELOPED FABRIC WEATHERED | REVERSE SIDE WEATHERED | |
| TACTEL® Deva Blue 9-420-6-1 10/0 | 3/159 | 8/159 | | After 159 hrs., enveloped fabric significantly less weathered than original; original nearly white; enveloped fabric still light blue. |
| TACTEL® Hot Correl 9-420-6-2 (AKA 18) 10/0 | 5/24 | 10/24 | 9/24 | After 24 hrs., enveloped fabric is significantly less weathered than original, as was reverse side. |

Example 30

Abrasion Resistance Testing

The results of abrasion resisting testing clearly show that enveloped fiber fabrics of this invention have superior wear characteristics compared to the untreated original (starting) fabrics. In most cases, the enveloped fiber fabric samples underwent twice as many cycles as the untreated samples without evidencing tearing in the samples. Such results can be explained by theorizing that the envelopment with silicone polymer of the yarns and fibers comprising a fabric, provides such treated yarns and fibers with a lubricity agent so that abrasive action was minimized and the integrity of the fabric was preserved significantly longer. The anti-abrasion characteristics also applied to the minimized effects of one fiber rubbing against another fiber, or of one yarn against another yarn.

This experiment compared the abrasion resistance of embodiments of the enveloped fiber fabrics of this invention with untreated fabrics. The durability of each fabric test specimen was determined by the Taber Abraser. Each specimen is abraded for the number of cycles indicated. Comparisons were then made between the enveloped fiber fabrics of the invention and untreated fabrics. Specifically, this test method utilizes the Taber Abraser No. 174. An important feature of this abrader was that its wheels traverse a complete circle on the test specimen surface. Thus, the surface was abraded at all possible angles relative to the weave or grain of the specimen. Comparisons of the enveloped fiber fabric to the untreated fabric were based upon a scale 0 through 10, where 0 was a completely torn specimen, and 10 was the new (or starting) sample.

Each test procedure used a single 7 inch diameter fiber enveloped fabric specimen, and a single 7 inch diameter

6. The abraser was started.

7. At the procedurally specified number of revolutions, the abraser was stopped and each fabric sample was rated at a value between 0 and 10.

Illustrative results of the test on some sample fabrics are shown in Table X.

Abrasion Testing

Numeric Grade of Abrasion 0-10

- 0—Total failure of fabric specimen. Fibers are torn apart
- 5—Fabric specimen is starting to tear. Fabric is noticeably thinner
- 10—Original unabrased fabric specimen

TABLE X

| SPECI- MENS | UNTREATED FABRIC | ENCAP- SULATED FABRIC | COMMENTS |
|----------------------|---------------------|-----------------------------|--|
| Hot Correl Tactel | 5 1,000 cyc. | 7 1,000 cyc. | Untreated sample is starting to tear, and enveloped sample was still intact. |
| Deva Blue Tactel | 4 1,000 cyc. | 7 1,000 cyc. | Visible rips in untreated sample. Enveloped sample shows were frayed. |

Example 31

Breathability Testing

This test procedure followed the Modified ASTM E96-8 test. As shown by the results of this testing in the following Table, the fiber enveloped fabrics of this invention were

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found to have high breathability. This breathability was in excess of that needed to remove the average value of several thousand grams of perspiration generated daily by the human body. The results for the fiber enveloped fabrics of this invention were generally superior to the corresponding results measured under the same conditions for prior art treated fabrics, such as the Gore-Tex® brand fabric.

Breathability of a fabric sample was determined by accurately weighing the amount of water passing through such fabric sample under carefully controlled temperature and relative humidity conditions in an environmental chamber. The water weight loss from a cup whose mouth is sealed with a fabric sample was expressed as grams of water vapor per square meter of fabric per 24 hour day.

In an attempt to more realistically simulate what is actually occurring inside the apparel during exercise, a specially designed test was performed to measure outward water vapor transport (MVTR) in a "Bellows" effect. The test simulates the high volumes of moisture and air that mix within a garment that pass outward through it as air is drawn in resultant from activity. The enveloped fabrics of this invention were found to provide increased performance at a higher activity, or air exchange level than is achievable with corresponding untreated fabrics.

The "Bellows" MVTR breathability test was run inside of a controlled temperature/humidity chamber similar to the foregoing cup test. However, instead of a standard cup, each fabric sample was sealed over the open top of a special cup which was provided with an air inlet aperture in its bottom, thereby allowing air to be bubbled up through the sealed container at a controlled rate. A check valve at the air inlet operation prevents backup or loss of water from the container. The air bubbles passed upwardly through the water and out through the fabric sample mounted sealingly across the cup top along with the water vapor. Table XI illustrates some representative results obtained.

TABLE XI

| Moisture Vapor Transport (MVTR) | |
|---|---------------------|
| FABRIC | MVTR ⁽¹⁾ |
| Made by a Method of the Invention Enveloped Fiber Fabric, Hot Core "Tinsel"® Commercial Product Gore-Tex®-Ply Fabric | 13,600 10,711 |

Table Footnote:

⁽¹⁾MVTR here references moisture vapor transport through a fabric sample as measured by the "Bellows" test with air delivered to the bubbler at 2 to 4 psi air pressure, in an Environmental Chamber at 100 to 102° F. and 35-45% relative humidity. MVTR is expressed as grams of water per square meter of surface per 24 hour day.

The MVTR data shown below is an example of a web where the fluorochemical is blooming from the fibers through the silicone thin film and re-orienting on the surface of the thin film. This data shows no significant reduction in moisture vapor transport rate with a fluorochemical additive on the surface of the silicone. The silicone polymer composition used was GE 6108 A:B (1:1), with 19.51% weight add-on, and the durable water repellent (DWR) was a fluorochemical composition that was added to the web as a pre-treatment.

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TABLE XII

MVTR Results of Web Treated with a Fluorochemical Additive

| FABRIC | MVTR (g/m ² · day) |
|--|-------------------------------|
| Untreated Versatec, Pulsion Print (M032195A1E) | 1581.67 |
| Treated Versatec • GE 6108 • DWR | 1444.99 |

Example 32

Water Repellency: Spray Testing

Water repellency spray testing is carried out according to AATCC Test Method 22-1974. The results of such testing show that the fiber enveloped Tactel®-type fabrics of the invention show excellent initial spray ratings initially, as do the original untreated fabrics which have been treated with water repellent chemicals such as fluorochemicals. Specifically, as the results shown below demonstrate, after ten machine washes, the treated side of a fiber enveloped fabric of the invention was found to remain highly water repellent, while, on the reverse side thereof, the original water repellency rating was found to have fallen significantly. The water repellency spray rating on the untreated fabric fell even more drastically. Excellent "hand" was retained after the test. It is believed that pretreatment with a fluorochemical having good water repellent properties can augment and even synergistically coact with the silicone resin used to produce fiber enveloped fabrics of this invention to produce superior spray ratings in such a fiber. The results are shown in Table XIII.

This test method is believed to be applicable to any textile fabric, whether or not it has been given a water resistant or water-repellent finish. The purpose of the test is to measure the resistance of fabrics to wetting by measuring the water-repellent efficiency of finishes applied to fabrics, particularly to plain woven fabrics. The portability and simplicity of the instrument, and the shortness and simplicity of the test procedure, make this method of test especially suitable for mill production control work. This test method is not intended, however, for use in predicting the probable rain penetration resistance of fabrics, since it does not measure penetration of water through the fabric.

The results obtained with this test method are believed to depend primarily on the resistance to wetting, or the water repellency, of the fibers and yarns comprising a fabric, and not upon the construction of the fabric. This test involves spraying water against the flat surface of a test fabric specimen under controlled conditions which produce a wetted pattern whose size depends on the relative water repellency of the fabric. Evaluation is accomplished by comparing the wetted pattern with pictures on a standard chart. The methods and apparatus and materials employed for this test were an AATCC Spray Tester, a beaker, distilled water, and the specimen fabrics.

The procedure followed for this test was as follows: a test specimen, which had been conditioned as procedurally directed, was fastened securely in a 15.2 cm (6") metal hoop so that it presented a smooth wrinkle-free surface. The hoop was then placed on the stand of the tester so that the fabric was uppermost in such a position that the center of the spray pattern coincided with the center of the hoop. In the case of (wills, gabardines, piques or fabrics of similar ribbed construction, the hoop was placed on the stand in such a way that the ribs were diagonal to the flow of water running off the fabric specimen.

250 milliliters (ml) of distilled water at 27° C ± 1° C. (80° F ± 2° F) was poured into the funnel of the tester and allowed

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to spray onto the test specimen, which took approximately 25 to 30 seconds. Upon completion of the spraying period, the hoop was taken by one edge and the opposite edge lapped smartly once against a solid object, with the fabric facing the object. The hoop was then rotated 180 degrees and then lapped once more on the location previously held.

The procedure and methods and apparatus of this test were slightly modified from the specifications, as follows:

1. The spray nozzle holes were slightly larger than specified, but the flow rate of the nozzle was 250 ml/30 sec., as required.

2. The number of taps of the hoop was two instead of one.

For each wash test, a fabric sample was washed using a warm wash/cold rinse cycle with one cup of Tide® detergent and dried at a hood/dry cycle in a dryer, unless otherwise indicated. The test results were evaluated by comparing the wet or spotted pattern on the fabric sample after tapping the hoop with the standard rating chart. Results produced surface wetting, with no water completely soaking through the test fabric sample. The numbers were ratings based upon the standard chart. Such values are thus subjective deductions by an experienced experimenter.

TABLE XIII

| ORIGINAL Fabric Type & Number | TREATED WEBS OF THE INVENTION | | | | |
|-------------------------------------|-------------------------------|---------------|----------------------|---------------|----------------------|
| | Initial | | After 100 Washes | | |
| | Initial | Appl. on Side | Non-Application Side | Appl. on Side | Non-Application Side |
| Supplier MO33194C | 100 | 100 | 100 | 70 | 80 |
| Mod Blue 4040 MO32994B-1E | 100 | 100 | 100 | 90 | 90 |
| Yellow 4040 MO33094B-1B | 100 | 100 | 100 | 90 | 90 |

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container which contains 700 ml of tap water. The fabric sample and the blotter sample are each then subjected to a continuous pressure of 87 lbs. distributed evenly over 100 square inches of surface area for a period of 30 minutes. After this time, a visual inspection of the fabric is made for any water penetration, and the paper blotter is weighed to detect water gain or penetration.

The methods and apparatus employed for each such test was one 20 inch diameter aluminum pan, one 87 lbs. weight distributed evenly over 100 square inches of fabric, one paper blotter, 700 ml water, miscellaneous fabric scraps for cushioning and the test fabric sample pieces.

Paper blotter dry weight: 4.7 gm

Total weight applied to fabric: 87 lbs.

Pressure evenly distributed over surface area of: 100 sq. in.

Pressure: 0.87 lbs./sq. in

The procedure observed for this test was as follows:

1. 700 ml tap water was placed in the round pan.
2. The fabric sample was placed with one side facing the water.
3. One piece of dry blotter paper was placed over the fabric to cover the pan.
4. Scrap fabric was placed over the blotter paper to cushion the weight.
5. The 87 lb. weight was distributed evenly over the 100-square-inch area.
6. This assembly was left undisturbed for 30 minutes.
- 7 After this time period, the visual results were recorded

TABLE XIV

| FABRIC SAMPLE AND THICKNESS | Fiber Enveloped Fabric of the Invention | | |
|------------------------------------|--|--|--|
| | ENVELOPED SIDE OF FABRIC FACING WATER | NON-ENVELOPED SIDE OF FABRIC FACING WATER | CONTROL FABRIC |
| Dark Blue Tide® 0.009 inches | No water penetration through the fabric. No visible water spots. Paper weight = 4.7 gm Water gain = 0.0 gm | No water penetration through the fabric. No visible water spots. Paper weight = 4.7 gm Water gain = 0.0 gm | Failure - total absorption of fabric and blotter. |

Example 33

Moisture Penetration Test

The results shown in the Table below demonstrate that all of the fiber enveloped fabrics of this invention test were significantly better than the original untreated fabrics with regard to resisting the penetration of water under the test conditions used. After the test, the "band" of the tested fabric samples remained excellent.

The purpose of this test was to evaluate how well a fabric stands up to wetness under continuous pressure, such as kneeling on the ground, or sitting in a wet chairlift, for a period of 30 minutes. This test involves placing both a fabric sample and a standard blotter sample on top of a water

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Example 34

Rain Test

In this testing, the rain test procedure of AATCC Method 35-1985 was followed.

The rain test results obtained demonstrate the clear superiority of the fiber enveloped fabric of the present invention as compared to the original untreated fabric. The data in the Table below shows that fiber enveloped fabrics pass this test by allowing virtually no water to pass therethrough. This result is comparable to the results obtained with higher cost so-called breathable waterproof fabrics currently commercially available in the market. In contrast, the original, untreated fabrics fail to pass this test because they demon-

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strate complete saturation. The fiber enveloped fabric samples retain excellent "hand" after the test.

The purpose and scope of this ASTM test is to evaluate resistance of a fiber enveloped fabric to water under simulated storm conditions. The test specifies that a test fabric is stormproof if less than one gram of water is absorbed by blotter paper with a shower head pressure of 3 feet exerted for 5 minutes. This test method is applicable to any textile fabric, whether or not it has a water repellent finish. It measures the resistance of a fabric to the penetration of water by impact, and thus can be used to predict the probable rain penetration resistance of a fabric. The results obtained with this method of test depend on the water repellency of the fibers and yarns in the fabric tested, and on the construction of the fabric.

This test involves a test specimen backed by a pre-weighed standard blotter. The assembly is sprayed with water for 5 minutes under controlled conditions. The blotter then is separated and weighed to determine the amount of water, if any, which has leaked through the specimen fabric during the test and has been absorbed by the blotter.

The methods and apparatus and materials employed in each test were a modified rain tester, blotter paper, water at 80° F.±2° F., a laboratory balance, 8"x8" fabric specimens which had been pre-conditioned in an atmosphere of 65% (±2%) relative humidity and 70° F. (±2° F.) for four hours before testing, and tape.

The procedure followed for this test was as follows:

1. A 6"x6" paper blotter was weighed to the nearest 0.1 gm and placed behind the test specimen.
2. The test fabric with the paper blotter in registration therewith was taped on the specimen holder.
3. A tube in the rain tester was filled with water up to the 3 foot level. It was confirmed that water was flowing out of the overflow tube which maintains the 3 foot column of water.
4. The water spray distance from the tip of the nozzle to the specimen holder was measured and adjusted to 12 inches.
5. The specimen holder was left in place and the rain tester was turned on for five minutes.
6. After the test period, the paper blotter was removed and reweighed to the nearest 0.1 gm.

The results of the test selected fabric samples are shown in Table XV.

TABLE XV

Rain Test—Criteria of Water Penetration the Fabric

| FABRIC SAMPLE | ORIGINAL NOT WASHED | AFTER 5 MACHINE WASHES | AFTER 10 MACHINE WASHES |
|-------------------------------|---------------------|------------------------|-------------------------|
| Hot Coral Tactel [®] | 0 | 0 | 0 |
| Deva Blue Tactel [®] | 0 | 0 | 0 |
| Prior Art Treated Fabric | | | |
| Ulrica [®] | 0 | — | 0.1 |
| Gore-Tex [®] | 0 | 0 | — |

Original Fabrics—Water Repellent Chemicals Only, No Encapsulation

Hot Coral Tactel/Failed-saturated

Deva Blue Tactel/Failed-saturated

It should be understood, of course, that the foregoing relates only to preferred embodiments of the present invention and that numerous modifications or alterations may be

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made therein without departing from the spirit and the scope of the invention as set forth in the appended claims.

That which is claimed is:

1. An article comprising a porous web that has been treated with a curable, shear thinnable, thixotropic polymeric material and with one or more modifiers, said material being at least partially cured, said modifiers being selectively positioned within the web, and at least some of the pores of said web being open.

2. The article of claim 1, wherein the modifier is selectively positioned substantially on one surface of the porous web.

3. The article of claim 1, wherein said modifier alters the functional properties of said article.

4. The article of claim 1, wherein said modifier is selected from biocides, therapeutic agents, adhesive agents, processing agents, humidity-controlling agents, water repellents, ion-exchange agents, light-reflective agents, dyes and pigments, mildew-resistance agents, conductive agents, proteins, hand-altering agents, blood repellents, flexibility-inducing agents, light fastness-inducing agents, rot-resistant agents, stain-resistant agents, grease-resistant agents, ultraviolet-absorbing agent, fillers, flattening agents, electrical conductive agents, thermal conductive agents, flame retardants, antistatic agents, sub-micron particulate matter, electromagnetic shielding agents or radio frequency shielding agents.

5. The article of claim 4, wherein the biocide is selected from halogen and halogen-based compounds, antibiotics, anti-virals, nonoxynol-9, phenols and phenolic compounds, quaternary ammonium salts, zinc oxide, Z-N-octyl-4-isothiazole-3-one, phenyl mercuric acetate, skin disinfectants, water disinfectants, air disinfectants, gaseous disinfectants, clothing disinfectants, methyl dimethyl propoxylene ammonium chloride, polyiodides, acid salts derived from hydrochloric, methanesulfonic, ethanesulfonic, isothionic, lactic or citric acids, or trichloro-carbon.

6. The article of claim 4, wherein the light reflective agent is selected from titanium oxide or zinc oxide.

7. The article of claim 4, wherein the mildew resistant agent is selected from thiazolylbenzimidazole, zinc phosphite, phenols, benzothiazoles or organosilicon quaternary ammonium salts.

8. The article of claim 4, wherein the hand-altering agent is selected from proteins or polyolefin fibers or fabrics.

9. The article of claim 4, wherein the filler is selected from carbon, molecular sieves, fumed silica or colloidal silica.

10. The article of claim 4, wherein the flame retardant is selected from aluminum hydroxide, borax, ictrakis (hydroxymethyl)phosphonium chloride, potassium hexafluoro zirconate, potassium hexafluoro titanate, polyamides, polyimides, poly-parabenic acid, polyether sulfones, polyether ether ketones, polyetherimides, fluoro-plastic resin films, polyphenylene sulfide, magnesium hydroxide, silicone-treated magnesium oxide, polybenzimidazole, flame-durable fibers, carbon or carbonizable compositions, retardant powder fillers, kaolin, gypsum, hydrated clay, polypropylene, polybutylene, metal carboxyl salts containing at least 6 carbon atoms, calcium compounds, barium atoms, strontium atoms, salts of inorganic acids, polyolefins, copolymers of polystyrene or polycarbonates, polyesters, polyamides, polycaprolactams, ionomers, polyurethanes, acrylonitrile-butadiene-styrene polymers, acetal resins, ethylene-vinylacetate resins, polymethylpentene, polyphenylene oxide, or polyphenylene oxide-polystyrene blends.

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11. The article of claim 4, wherein the ultraviolet absorbing agent is selected from benzophenones, benzotriazoles, cinnamic acid esters, benzoxazoles, 4-thiazolidones, titanium dioxide or zinc oxide.

12. The article of claim 4, wherein the antistatic agent is selected from fatty acid esters and their derivatives, long-chain alcohols, amides, quaternary ammonium salts, polyoxyethylene derivatives, polyglycols and their derivatives, polyhydric alcohols and their derivatives or epoxides and glycol ethers thereof.

13. The article of claim 4, wherein said processing agent is selected from cross-linking inhibitors, rheological agents, polyvinyl alcohol or hydrophilic polymers.

14. The article of claim 1, wherein said modifier contains reactively available sites.

15. The article of claim 14, wherein the reactively available sites of the modifier are oriented outwardly from a surface of the porous web.

16. The article of claim 14, wherein said reactively available sites are capable of binding an agent.

17. The article of claim 14, wherein said modifier is selected from polyurethane, phenolic resins, polyurea resins, polyololins, polyamides, polysiloxanes, polysulfides, polyvinyl esters or polyacetal resins.

18. The article of claim 16, wherein said modifier is polyurethane.

19. The article of claim 18, wherein said agent is iodine.

20. The article of claim 16, wherein said agent is an airborne organic contaminant.

21. The article of claim 14, wherein said modifier is biologically active.

22. The article of claim 21, wherein said biologically active modifier is selected from proteins, antibodies or enzymes.

23. The article of claim 16, wherein said agent is biologically active.

24. The article of claim 23, wherein said biologically active agent is selected from proteins, antibodies or enzymes.

25. The article of claim 14, wherein said reactively available sites catalyze a chemical reaction.

26. The article of claim 14, wherein said reactively available sites are capable of binding one or more proteins.

27. The article of claim 14, wherein said reactive sites are capable of binding one or more antibodies.

28. The article of claim 1, wherein said modifier promotes adhesion between the curable, thixotropic material containing one or more modifiers therein and the web.

29. The article of claim 1, wherein the modifier alters the surface chemistry of the article.

30. The article of claim 29, wherein said surface chemistry modifier is selected from the group consisting of fluorochemical compounds, proteins, anti-static agents, blood repellants, grease resistant agents.

31. The article of claim 1, wherein said modifier promotes the release of an agent from the web.

32. The article of claim 31, wherein said agent is a biologically active compound.

33. The article of claim 32, wherein the modifier is a hydrogel.

34. The article of claim 32, wherein the modifier is a fluorochemical compound.

35. The article of claim 1, wherein said thixotropic material comprises a polymer selected from polysiloxanes, polyurethanes, fluorosiloxanes, modified polyurethane silicones, modified silicone polyurethanes, acrylics or polytetrafluoroethylene.

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36. The article of claim 1, wherein said curable, thixotropic material containing one or more modifiers therein comprises a diluent.

37. The article of claim 36, wherein said diluent is selected from the group consisting of water, low molecular weight silicones, low molecular weight ketones or aromatics.

38. The article of claim 1, wherein said web is flexible.

39. The article of claim 1, wherein said web is rigid.

40. The article of claim 1, wherein said web is selected from foam, paper, leather or filtration membrane.

41. The article of claim 1, wherein said porous web is a fabric.

42. The article of claim 41, wherein said fabric is a woven fabric.

43. The article of claim 41, wherein said fabric comprises natural fibers.

44. The article of claim 41, wherein said fabric comprises synthetic fibers.

45. The article of claim 41, wherein said fabric is a non-woven fabric.

46. The article of claim 1, wherein said curable, thixotropic material and one or more modifiers forms a discontinuous film.

47. A porous article comprising:

a porous web having a plurality of web members with interstices therebetween;

at least partially cured material derived from a curable, shear thinnable, thixotropic polymeric material which forms:

a thin film substantially encapsulating at least some of the web members leaving at least some of the interstices open; or

a substantially continuous internal layer; and

one or more modifiers, wherein said modifier(s) is selectively positioned within the web.

48. The article of claim 47, wherein the modifier is selectively positioned substantially on one surface of the porous web.

49. The article of claim 47, wherein the modifier is selectively positioned substantially within the encapsulated material.

50. The article of claim 47, wherein the modifier is selectively positioned substantially on one surface of the encapsulated material.

51. The article of claim 47, wherein said modifier(s) projects through the surface of the encapsulated material.

52. The article of claim 47, wherein the substantially continuous internal layer is positioned close to a surface of the porous web.

53. The article of claim 47, wherein the modifier is selectively positioned substantially on one surface of the substantially continuous internal layer.

54. The article of claim 47, wherein the modifier is selectively positioned substantially within the substantially continuous internal layer.

55. The article of claim 47, wherein said modifier alters the functional properties of said article.

56. The article of claim 47, wherein said modifier is selected from biocides, therapeutic agents, adhesive agents, processing agents, humidity-controlling agents, water repellents, ion-exchange agents, light-reflective agents, dyes and pigments, mildew-resistance agents, conductive agents, proteins, hand-altering agents, blood repellents, flexibility-inducing agents, light fastness-inducing agents, rot-resistant agents, stain-resistant agents, grease-resistant agents, ultraviolet-absorbing agents, fillers, flattening agents, elec-

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trical conductive agents, thermal conductive agents, flame retardants, anti-static agents, sub-micron particulate matter, electromagnetic shielding agents or radio frequency shielding agents.

57. The article of claim 56, wherein the biocide is selected from halogens and halogen-based compounds, antibiotics, anti-virals, oodoxynol-9, phenols and phenolic compounds, quaternary ammonium salts, zinc oxide, Z-N-octyl-4-isothiazole-3-one, phenyl mercuric acetate, skin disinfectants, water disinfectants, air disinfectants, gaseous disinfectants, clothing disinfectants, methyl dimethyl propylene ammonium chloride, polyiodides, acid salts derived from hydrochloric, metanesulfonic, ethanesulfonic, isothionic, lactic or citric acids, or trichlorocarbox.

58. The article of claim 56, wherein the light reflective agent is selected from titanium oxide or zinc oxide.

59. The article of claim 56, wherein the mildew resistant agent is selected from thiazolylbenzimidazole, zinc phosphite, phenols, benzothiazoles or organosilicon quaternary ammonium salts.

60. The article of claim 56, wherein the band-altering agent is selected from proteins or polyolefin fibers or fabrics.

61. The article of claim 56, wherein the filler is selected from carbon, molecular sieves, fumed silica or colloidal silica.

62. The article of claim 56, wherein the flame retardant is selected from aluminum hydroxide, borax, tetrakis (hydroxymethyl)phosphonium chloride, potassium hexafluoro zirconate, potassium hexafluoro titanate, polyamides, polyimides, poly-parahanic acid, polyether sulfones, polyether ether ketones, polyetherimides, fluoroplastic resin films, polyphenylene sulfide, magnesium hydroxide, silicone-treated magnesium oxide, polybenzimidazole, flame-durable fibers, carbon or carbonizable compositions, retardant powder fillers, kaolin, gypsum, hydrated clay, polypropylene, polybutylene, metal carboxyl salts containing at least 6 carbon atoms, calcium compounds, barium atoms, strontium atoms, salts of inorganic acids, polyolefins, copolymers of polystyrene or polycarbonates, polyesters, polyamides, polycaprolactams, ionomers, polyurethanes, acrylonitrile-butadiene-styrene polymers, acetal resins, ethylene-vinylacetate resins, polymethylpentene, polyphenylene oxide, or polyphenylene oxide-polystyrene blends.

63. The article of claim 56, wherein the ultraviolet absorbing agent is selected from benzophenones, benzotriazoles, cinnamic acid esters, benzoxazoles, 4-thiazolidones, titanium dioxide or zinc oxide.

64. The article of claim 56, wherein the anti-static agent is selected from fatty acid esters and their derivatives, long-chain amides, amides, quaternary ammonium salts, polyoxyethylene derivatives, polyglycols and their derivatives, polyhydric alcohols and their derivatives or epoxides and glycol ethers thereof.

65. The article of claim 56, wherein said processing agent is selected from cross-linking inhibitors, rheological agents, polyvinyl alcohol or hydrophilic polymers.

66. The article of claim 47, wherein said modifier contains reactively available sites.

67. The article of claim 66, wherein the reactively available sites of the modifier are oriented outwardly from a surface of the porous web.

68. The article of claim 66, wherein said reactively available sites are capable of binding an agent.

69. The article of claim 66, wherein said modifier is selected from polyurethane, phenolic resins, polyurea resins,

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polyolefins, polyamides, polysiloxanes, polysulfides, polyvinyl esters or polyacetal resins.

70. The article of claim 69, wherein said modifier is polyurethane.

71. The article of claim 70, wherein said agent is iodine.

72. The article of claim 69, wherein said agent is an airborne organic contaminant.

73. The article of claim 66, wherein said modifier is biologically active.

74. The article of claim 73, wherein said biologically active modifier is selected from proteins, antibodies or enzymes.

75. The article of claim 68, wherein said agent is biologically active.

76. The article of claim 73, wherein said biologically active agent is selected from proteins, antibodies or enzymes.

77. The article of claim 66, wherein said reactively available sites catalyze a chemical reaction.

78. The article of claim 66, wherein said reactively available sites are capable of binding one or more proteins.

79. The article of claim 66, wherein said reactive sites are capable of binding one or more antibodies.

80. The article of claim 47, wherein said modifier promotes adhesion between the curable, shear thixotropic material containing one or more modifiers therein and the web.

81. The article of claim 47, wherein the modifier alters the surface chemistry of the article.

82. The article of claim 81, wherein said surface chemistry modifier is selected from the group consisting of fluorocarbon compounds, proteins, anti-static agents, blood repellants or grease resistant agents.

83. The article of claim 47, wherein said modifier promotes the release of an agent from the web.

84. The article of claim 83, wherein said agent is a biologically active compound.

85. The article of claim 84, wherein the modifier is a hydrogel.

86. The article of claim 84, wherein the modifier is a fluorocarbon compound.

87. The article of claim 47, wherein said thixotropic material comprises a polymer selected from polysiloxanes, polyurethanes, fluorosilicones, modified polyurethane silicones, modified silicone polyurethanes, acrylics or polytetrafluoroethylene.

88. The article of claim 47, wherein said curable, thixotropic material containing one or more modifiers therein comprises a diluent.

89. The article of claim 88, wherein said diluent is selected from the group consisting of water, low molecular weight silicones, low molecular weight ketones or aromatics.

90. The article of claim 47, wherein said web is flexible.

91. The article of claim 47, wherein said web is rigid.

92. The article of claim 47, wherein said web is selected from foam, paper, leather, filtration membrane, or laminate.

93. The article of claim 47, wherein said porous web is a fabric.

94. The article of claim 93, wherein said fabric is a woven fabric.

95. The article of claim 93, wherein said fabric comprises natural fibers.

96. The article of claim 93, wherein said fabric comprises synthetic fibers.

97. The article of claim 93, wherein said fabric is a non-woven fabric.

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98. The article of claim 47, wherein said curable, thixotropic material and one or more modifiers forms a discontinuous film.

99. The article of claim 47, wherein said internal layer has a thickness in the range of 0.01 micron up to 50 microns.

100. The article of claim 47, wherein said porous internal layer has a pore size of up to about 10 microns.

101. The article of claim 47, wherein the thickness of the thin film varies in a controlled gradient through the thickness of the web.

102. The article of claim 1, wherein the modifier is localized on one surface of the porous web.

103. The article of claim 47, wherein the modifier is localized at one or more selected positions within the web.

104. The article of claim 47, wherein the modifier is localized on one surface of the porous web.

105. The article of claim 47, wherein the modifier is localized within the encapsulated material.

106. The article of claim 47, wherein the modifier is localized on one surface of the encapsulated material.

107. The article of claim 106, wherein the modifier projects through the surface of the encapsulated material.

108. The article of claim 47, wherein the modifier is localized on one surface of the substantially continuous internal layer.

109. The article of claim 47, wherein the modifier is localized within the substantially continuous internal layer.

110. A method of controllably applying a combination of treating materials to a porous web, said method comprising: applying a curable shear thinnable, thixotropic material to said porous web,

applying one or more modifiers to said porous web; and subjecting said thixotropic material and modifier(s) to sufficient energy to cause the thixotropic material and modifier(s) to flow into the porous web, and selectively position said modifier(s) within the web, wherein at least some of the interstitial spaces of said web remain open.

111. The method according to claim 110 wherein said web is pretreated with said modifier, prior to applying said curable, thixotropic material thereto.

112. The method according to claim 110 wherein said modifier and said curable, thixotropic material are applied to said web in combination.

113. The method according to claim 110 wherein said modifier is applied to said web after applying said curable, thixotropic material thereto.

114. The method according to claim 113 wherein said curable, thixotropic material is subjected to shear thinning conditions prior to application of said modifier to said web.

115. The method according to claim 114 wherein said modifier is pressured into the web.

116. The method according to claim 110, wherein said thixotropic material and said modifier(s) are applied to the surface of the porous web.

117. The method according to claim 110, wherein said modifier alters the functional properties of the resulting article.

118. The method according to claim 110, wherein said modifier alters the functional properties of said curable, thixotropic material containing one or more modifiers therein.

119. The method according to claim 110, wherein said modifier is selected from the group consisting of biocides, therapeutic agents, adhesive agents, humidity-controlling agents, water repellents, ion-exchange agents, light-reflective agents, dyes and pigments, mildew-resistant

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agents, conductive agents, proteins, blood-altering agents, blood repellents, flexibility-inducing agents, light fastness-inducing agents, rot-resistant agents, stain-resistant agents, grease-resistant agents, ultraviolet-absorbing agent, fillers, flattening agents, electrical conductive agents, thermal conductive agents, flame retardants, antistatic agents, processing agents, electromagnetic shielding agents, and radio frequency shielding agents.

120. The method according to claim 110, wherein said modifier contains reactively available sites.

121. The method according to claim 120, wherein said reactively available sites are capable of binding an agent.

122. The method according to claim 118, wherein said curable, thixotropic material comprises a diluent.

123. The method according to claim 122, wherein said diluent is selected from the group consisting of water, low molecular weight silicones, low molecular weight ketones or aromatics.

124. The method according to claim 122, where said energy is sufficient to drive the diluent from the curable, thixotropic material.

125. The method according to claim 110, wherein said porous web has a plurality of web members with interstices therebetween and wherein the curable, thixotropic material and one or more modifiers forms a thin film substantially encapsulating at least some of the web members.

126. The method according to claim 110, wherein said porous web has a plurality of web members with interstices therebetween and wherein the curable, thixotropic material and one or more modifiers forms a substantially continuous, internal layer.

127. The method according to claim 125, wherein the curable, thixotropic material and one or more modifiers further form a substantially continuous, internal layer.

128. The method according to claim 125, wherein said energy causes a variation in thin film thickness in a controlled gradient through the thickness of the web.

129. The method according to claim 126, wherein the internal continuous layer is positioned close to the application surface of the porous web.

130. The method according to claim 126, wherein the internal continuous layer is positioned close to the surface opposing the application surface of the porous web.

131. The method according to claim 110, wherein the modifier is selectively positioned substantially on the application surface of the porous web.

132. The method according to claim 110, wherein the modifier is selectively positioned substantially on the surface opposing the application surface of the porous web.

133. The method according to claim 125, wherein the modifier is selectively positioned substantially within the encapsulated material.

134. The method according to claim 125, wherein the modifier is selectively positioned substantially on one surface of the encapsulated material.

135. The method according to claim 125, wherein said modifier(s) projects through the surface of the encapsulated material.

136. The method according to claim 126, wherein the modifier is selectively positioned substantially on one surface of the internal, continuous layer.

137. The method according to claim 126, wherein the modifier is selectively positioned substantially within the internal, continuous layer.

138. The method according to claim 120, wherein the reactive sites of the modifier are oriented outwardly from a surface of the porous web.

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139. The method according to claim 110, wherein said energy is provided by subjecting the curable, thixotropic material containing one or more modifiers therein and web to shearing conditions.

140. The method according to claim 130, wherein the shearing conditions are provided by passing the web and curable, thixotropic material containing one or more modifiers therein in contact with one or more blades at a predetermined angle with respect to the blades.

141. The method according to claim 140, wherein one or more of the blades is flexible.

142. The method according to claim 140, wherein one or more of the blades is rigid.

143. The method according to claim 139, wherein the shearing conditions are provided by passing the web and curable, thixotropic material containing one or more modifiers therein through rollers at a controllable pressure.

144. The method according to claim 110, further comprising at least partially curing said thixotropic material.

145. The method according to claim 144, wherein the energy for curing is provided by thermal energy, electron beam, microwave, electromagnetic radiation or ultrasonic energy.

146. The method according to claim 110, wherein said porous web comprises carpet fibers.

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147. The method according to claim 146, wherein said carpet fibers are combed prior to applying said curable, thixotropic composition and one or more modifiers thereto, and once again prior to curing the composition after shear thinning thereof.

148. The method according to claim 110, wherein the modifier is localized on the application surface of the porous web.

149. The method according to claim 110, wherein the modifier is localized on the surface opposing the application surface of the porous web.

150. The method according to claim 125, wherein the modifier is localized within the encapsulated material.

151. The method according to claim 125, wherein the modifier is localized on the surface of the encapsulated material.

152. The method according to claim 125, wherein the modifier projects through the surface of the encapsulated material.

153. The method according to claim 126, wherein the modifier is localized on one surface of the internal continuous layer.

154. The method according to claim 126, wherein the modifier is localized within the internal continuous layer.

* * * * *

EXHIBIT E



US006129978A

United States Patent [19]**Caldwell**[11] **Patent Number:** **6,129,978**[45] **Date of Patent:** ***Oct. 10, 2000**[54] **POROUS WEBS HAVING A POLYMER COMPOSITION CONTROLLABLY PLACED THEREIN**[75] **Inventor:** **J. Michael Caldwell, Cardiff, Calif.**[73] **Assignee:** **Nextec Applications, Inc., Vista, Calif.**[*] **Notice:** This patent is subject to a terminal disclaimer.[21] **Appl. No.:** **08/963,636**[22] **Filed:** **Nov. 3, 1997****Related U.S. Application Data**

[60] Division of application No. 08/407,191, Mar. 17, 1995, Pat. No. 5,876,792, which is a continuation-in-part of application No. 08/017,855, Feb. 16, 1993, Pat. No. 5,418,051, which is a continuation of application No. 07/680,645, Apr. 2, 1991, Pat. No. 5,209,965, which is a continuation of application No. 07/319,778, Mar. 10, 1989, Pat. No. 5,004,643, which is a continuation-in-part of application No. 07/167,630, Mar. 14, 1988, abandoned, which is a continuation-in-part of application No. 07/167,643, Mar. 14, 1988, abandoned, which is a continuation-in-part of application No. 07/167,797, Mar. 14, 1988, abandoned, which is a continuation-in-part of application No. 07/167,840, Mar. 14, 1988, abandoned.

[51] **Int. Cl. 7** **B32B 7/02**[52] **U.S. Cl.** **428/213; 428/308.4; 428/319.3; 442/281; 442/381; 442/417**

[58] **Field of Search** **428/212, 213, 428/304.4, 308.4, 319.3; 442/204, 205, 206, 207, 239, 268, 64, 65, 67, 59, 281, 417, 381**

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Primary Examiner—Blaine Copenbeaver*Assistant Examiner*—Uls C. Ruddock*Attorney, Agent, or Firm*—Karl Strauss; Lyon & Lyon, LLP[57] **ABSTRACT**

The present invention relates to a porous web comprising a plurality of structural elements with interstitial spaces therebetween, wherein at least some of the structural elements of the top and bottom surfaces of the web are encapsulated by a cured, shear thinned polymer composition and most of the interstitial spaces are open. The invention also relates to a porous web having a substantially contiguous region of a cured, shear thinned polymer composition extending through the web so that the polymer composition fills the interstitial spaces and adheres adjacent structural elements of the web in the region. In the areas of the web above and below the filled region, at least some of the structural elements are encapsulated and most of the interstitial spaces are open.

70 Claims, 21 Drawing Sheets

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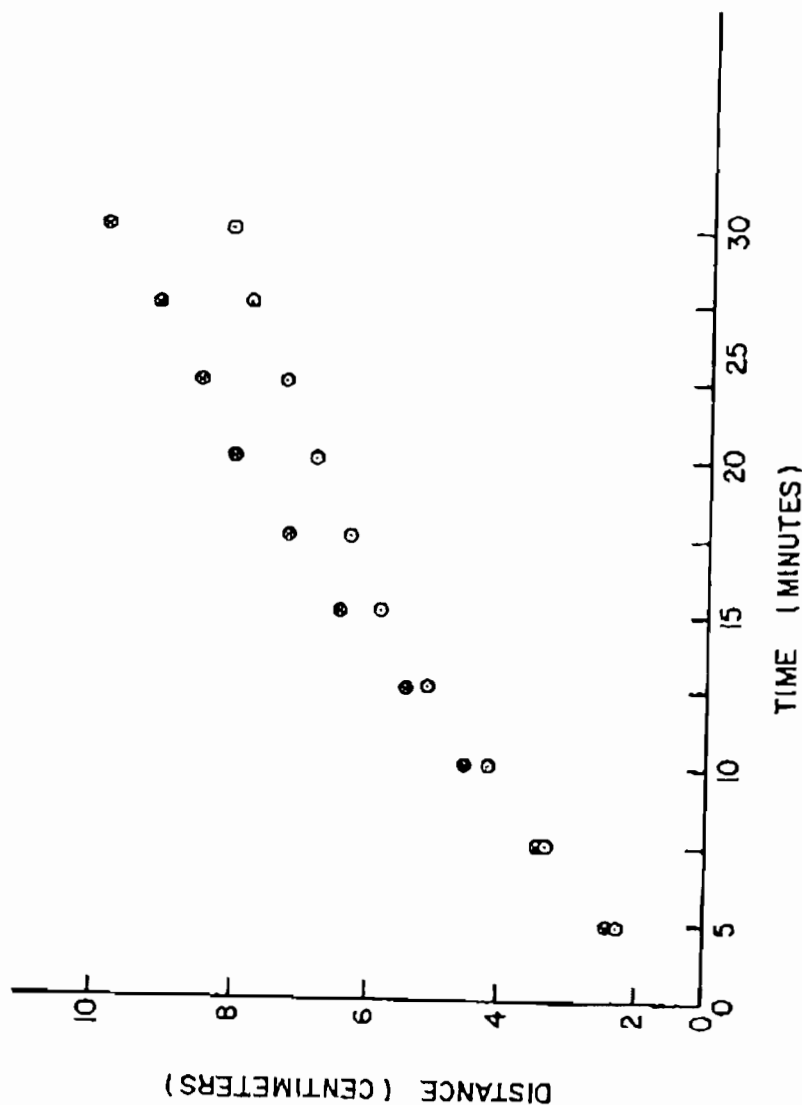


FIG. 1

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FIG. 2

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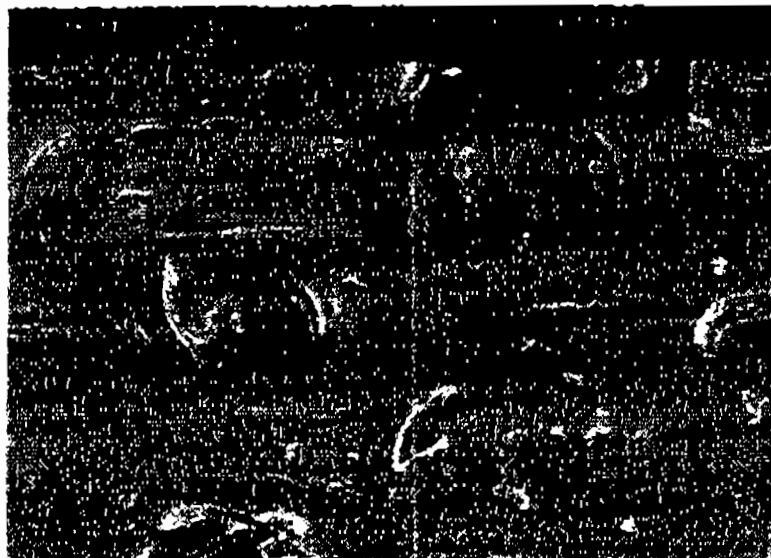


FIG. 3a



FIG. 3b

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FIG. 3c

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FIG. 4a

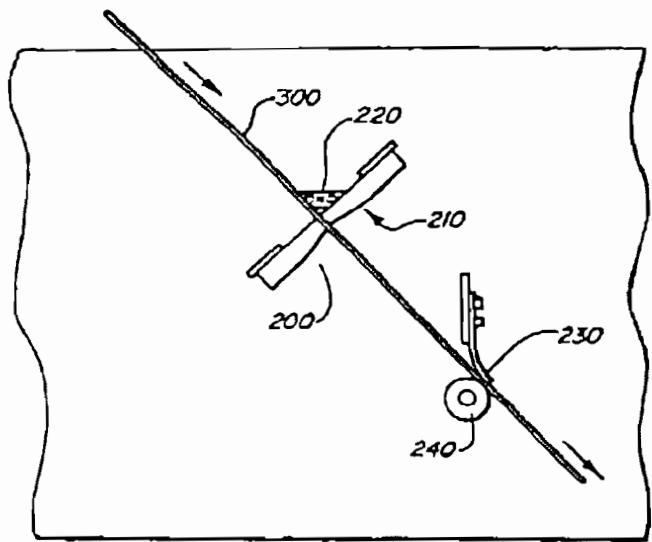
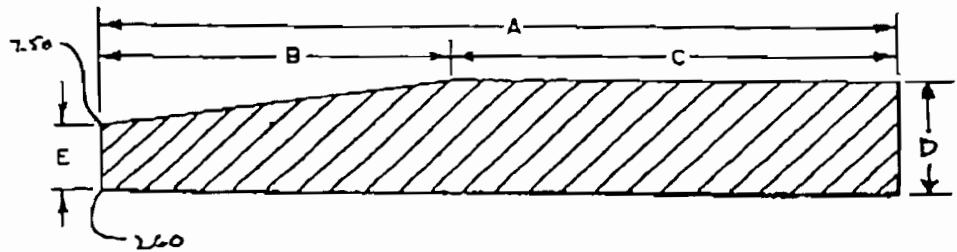


FIG. 4b



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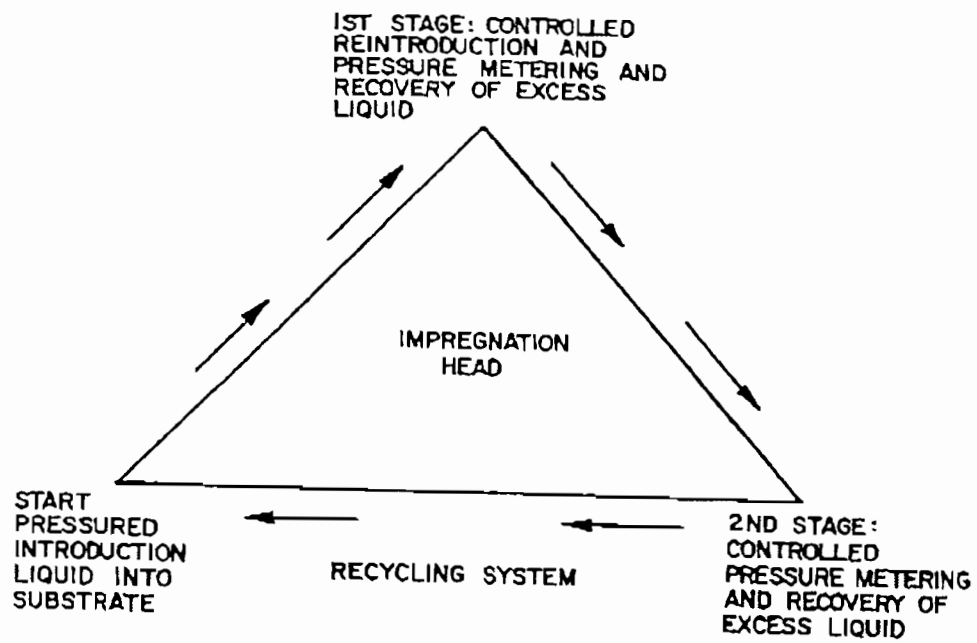


FIG. 5

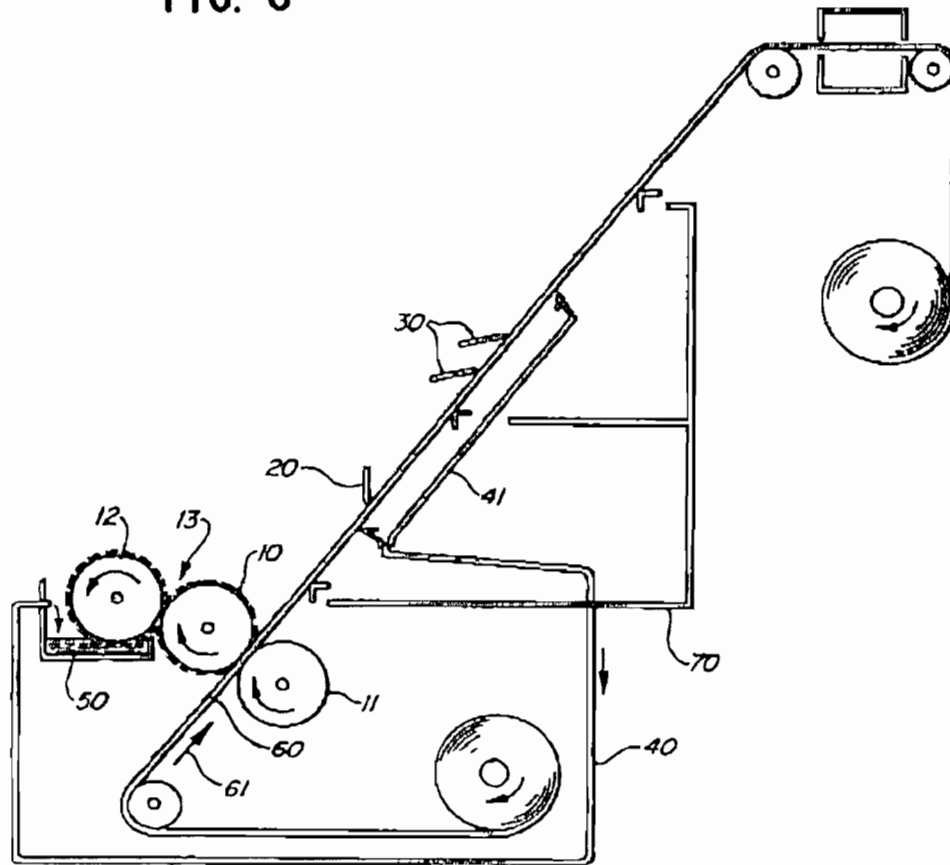
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FIG. 6



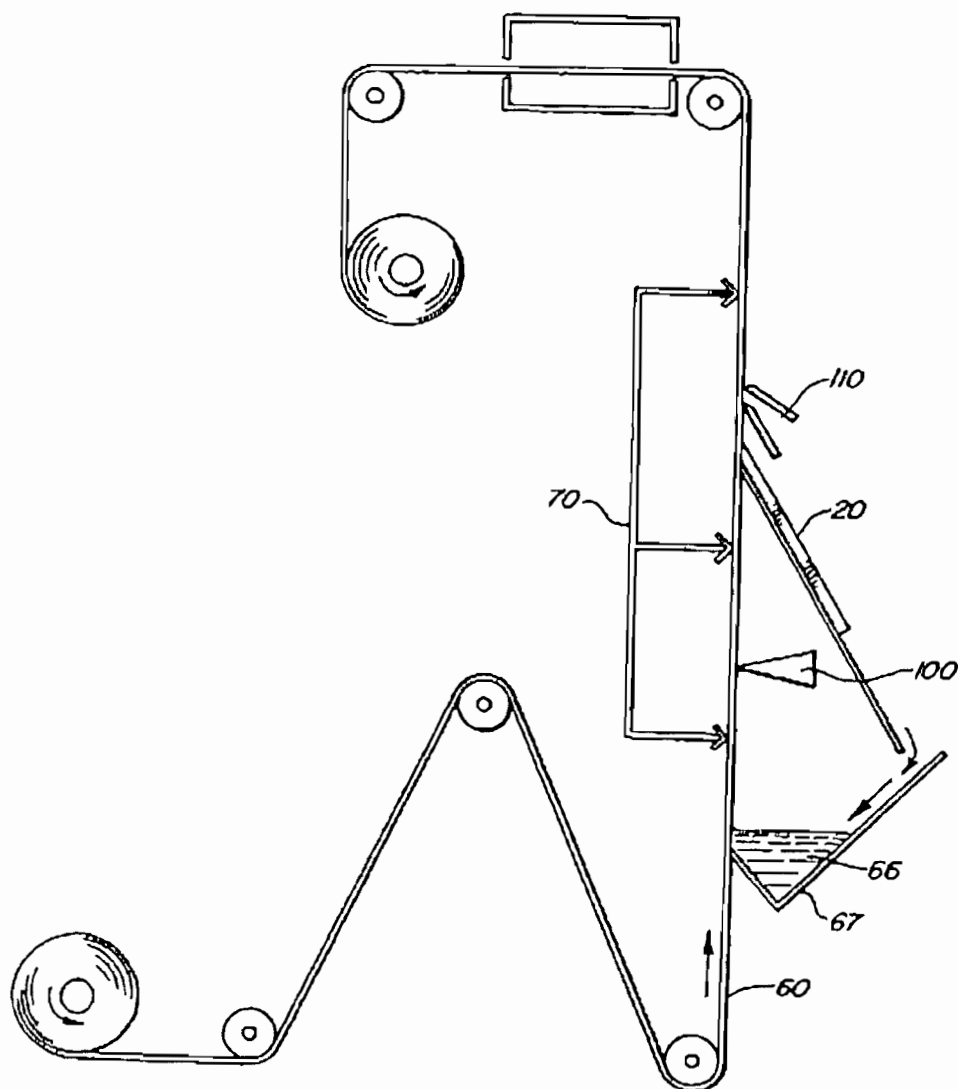
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FIG. 7



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FIG. 8a PRIOR ART

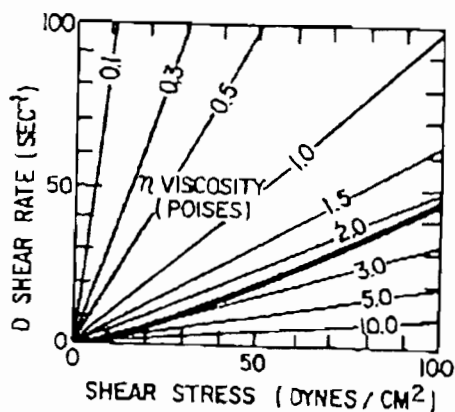


FIG. 8b PRIOR ART

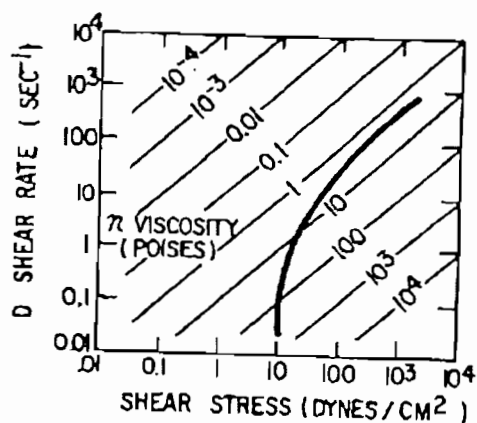


FIG. 8c PRIOR ART

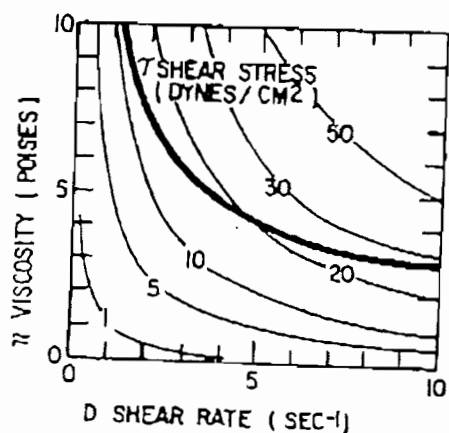
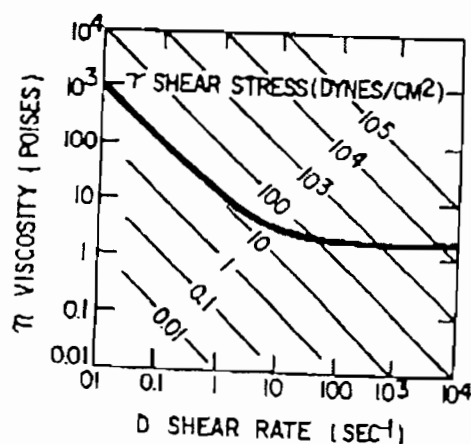


FIG. 8d PRIOR ART



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FIG. 9 PRIOR ART

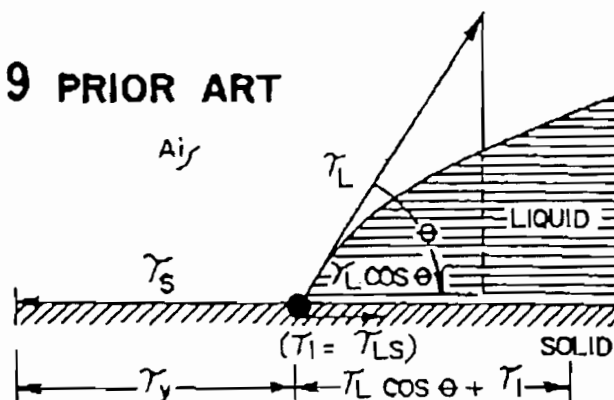
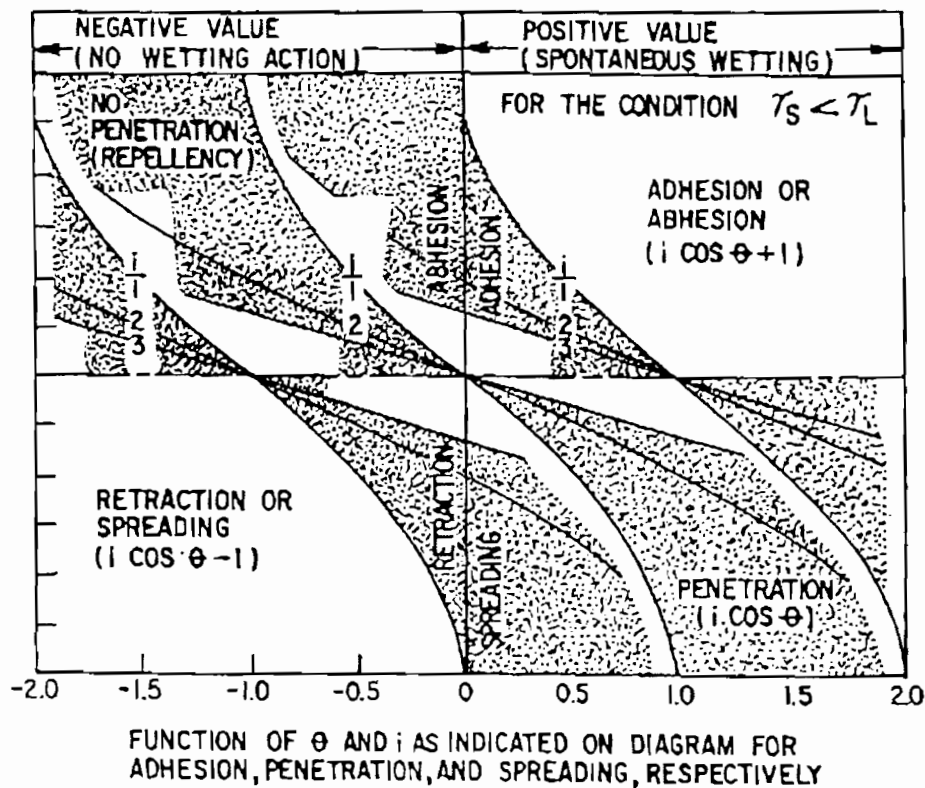


FIG. 10 PRIOR ART



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FIG. 11a PRIOR ART

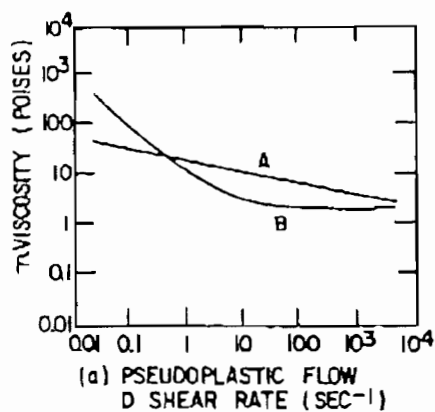


FIG. 11b PRIOR ART

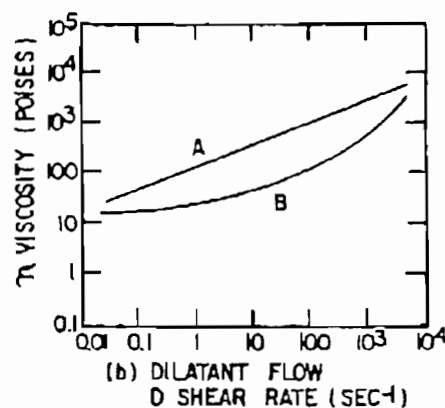


FIG. 11c PRIOR ART

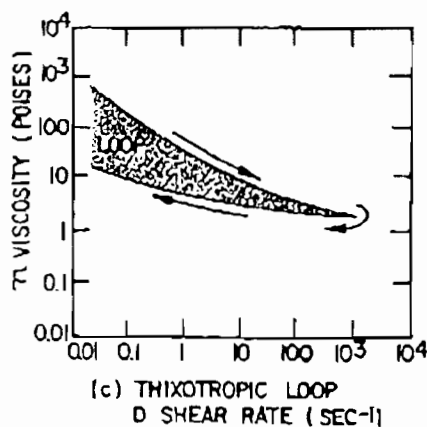
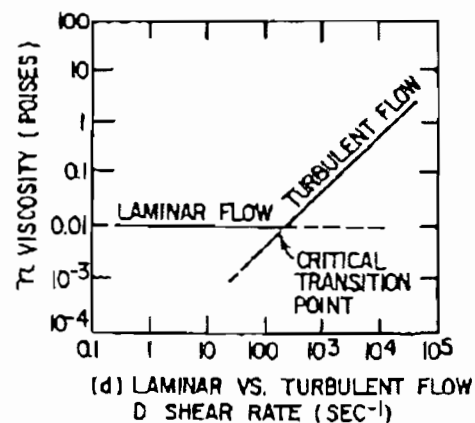


FIG. 11d PRIOR ART

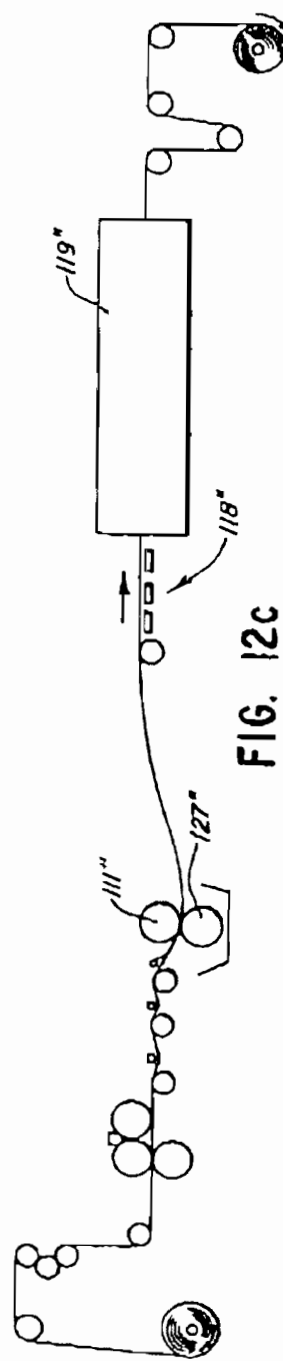
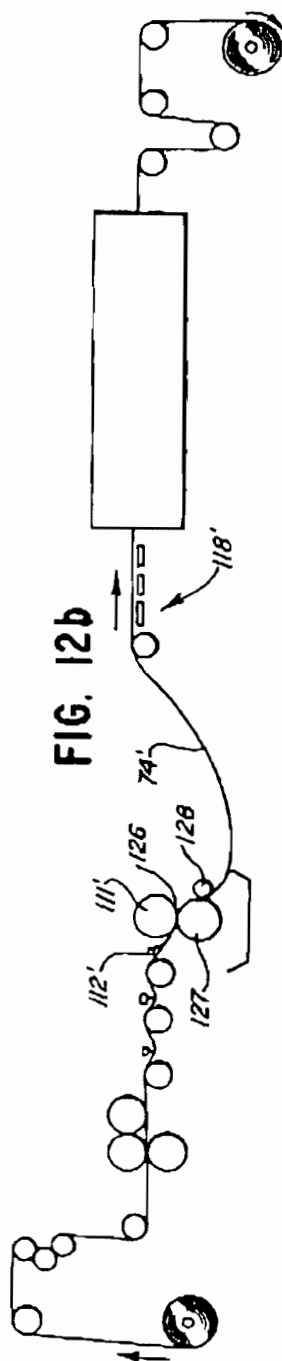
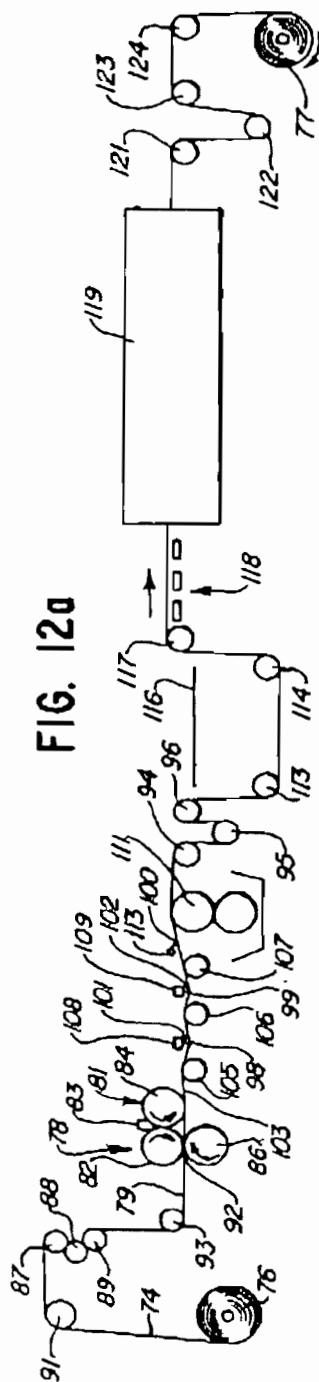


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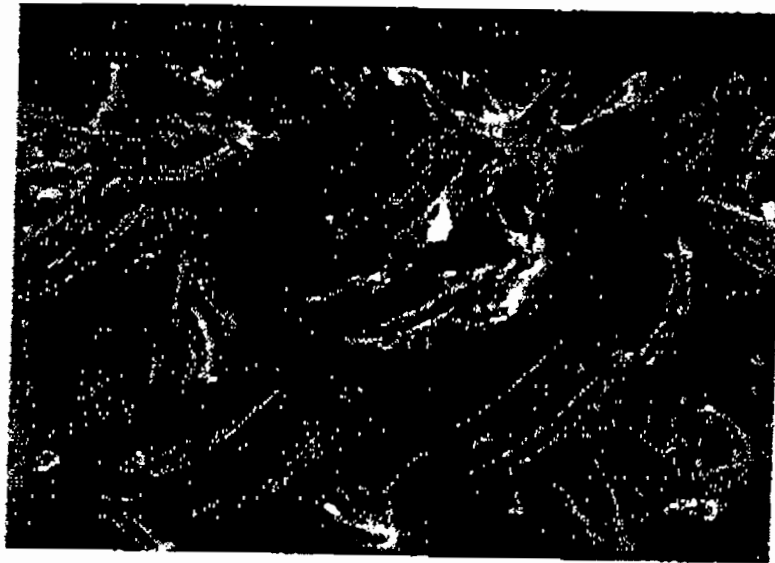


FIG. 13a



FIG. 13b

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FIG. 13c

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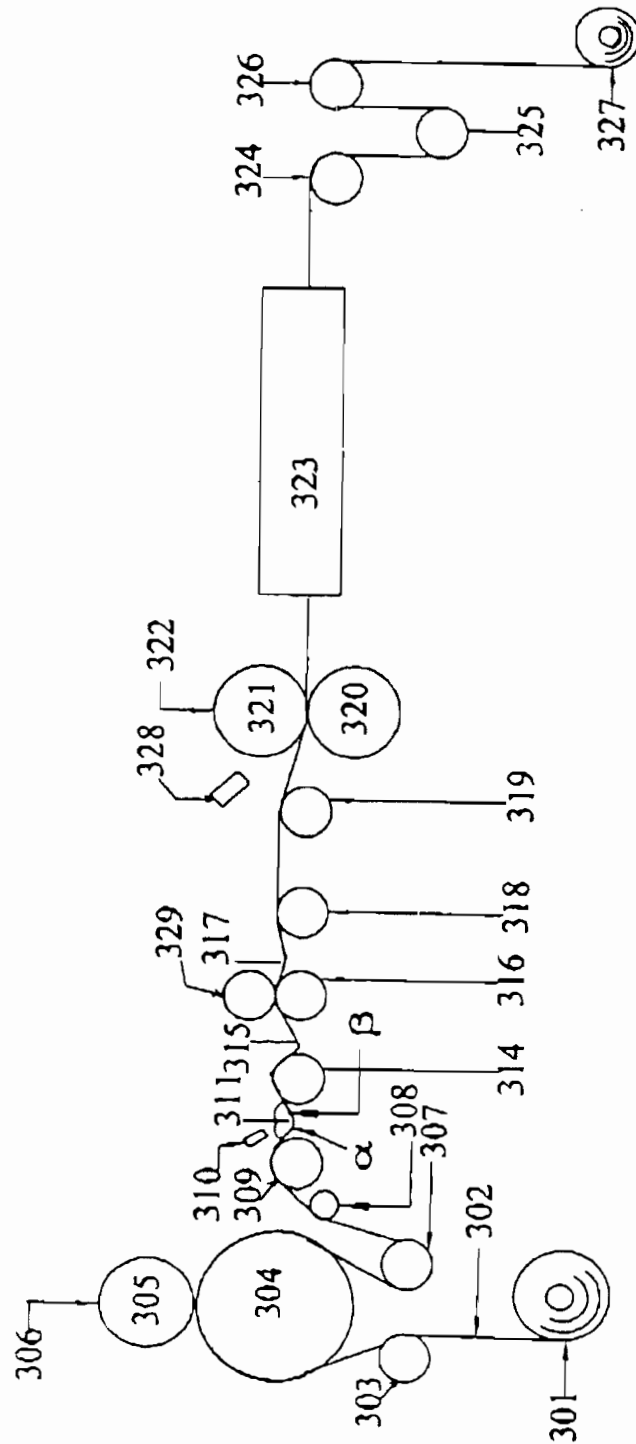


FIG. 14

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FIG. 15a

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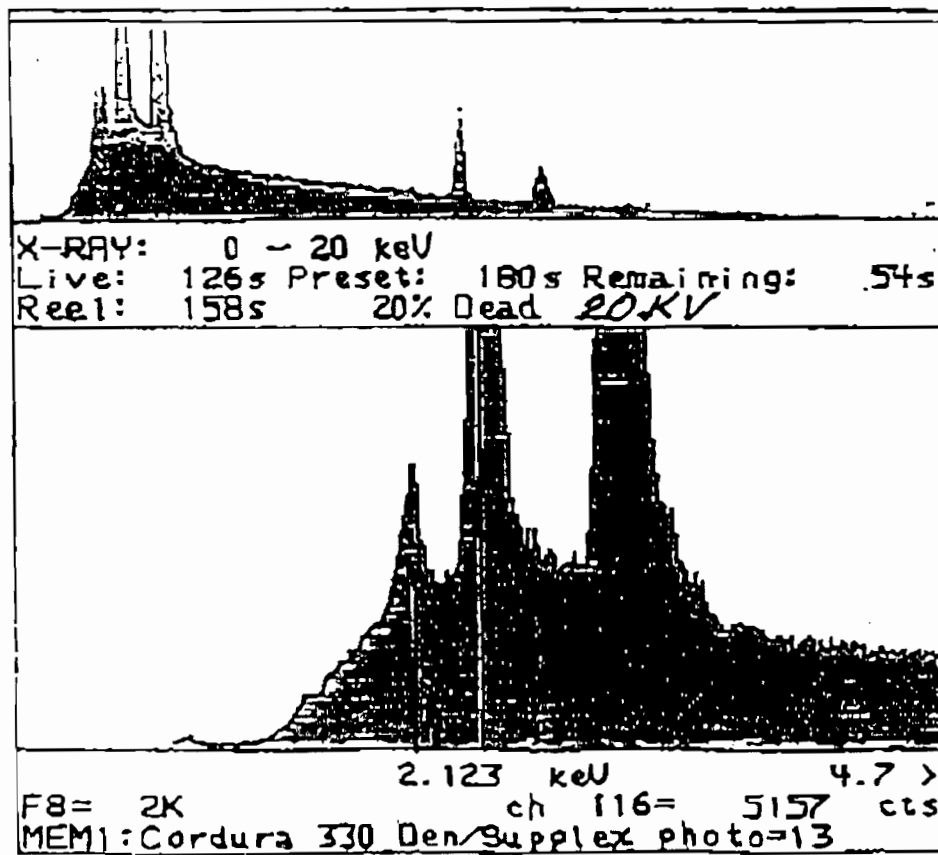


FIG. 15b

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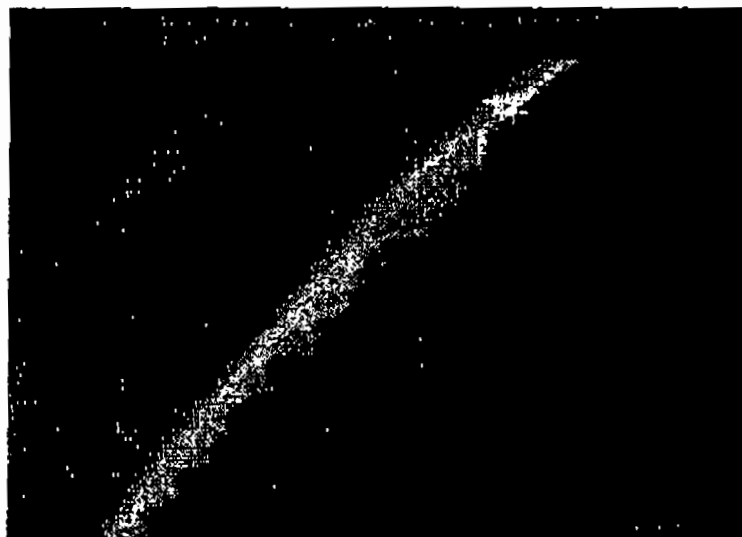


FIG. 15c



FIG. 15d

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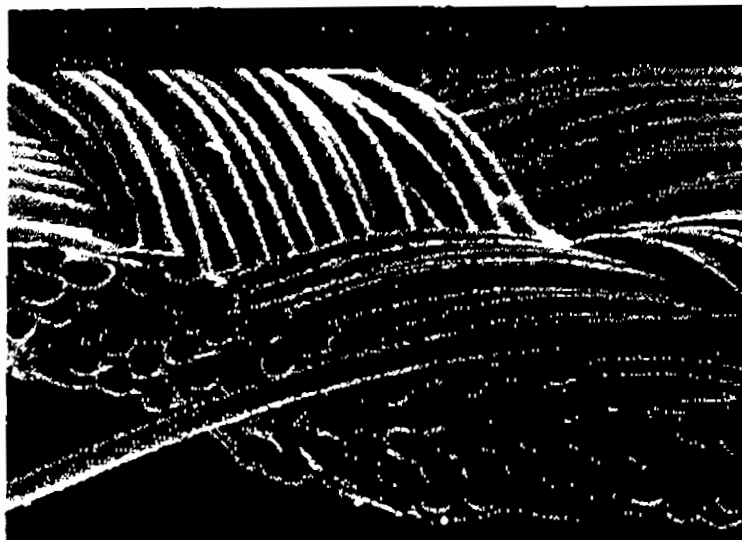


FIG. 15e

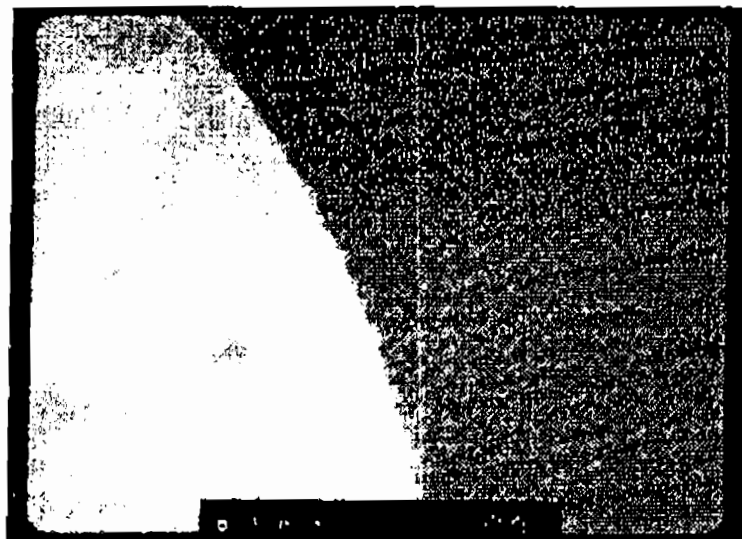


FIG. 15f

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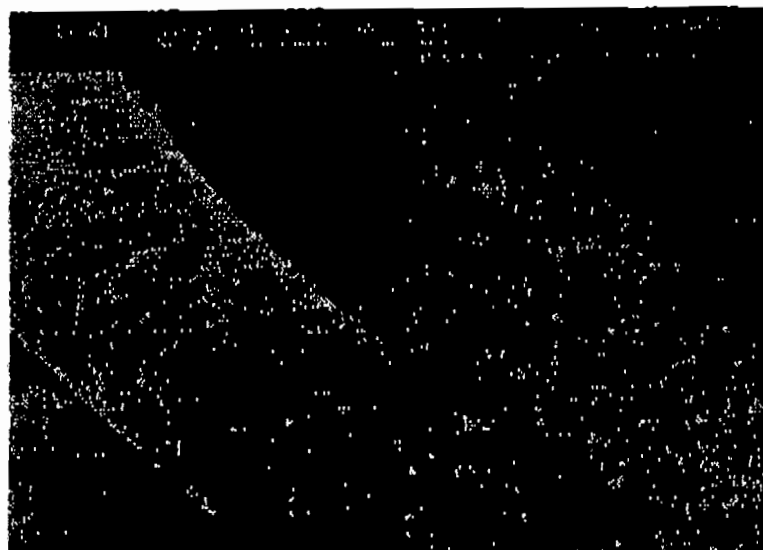


FIG. 15g

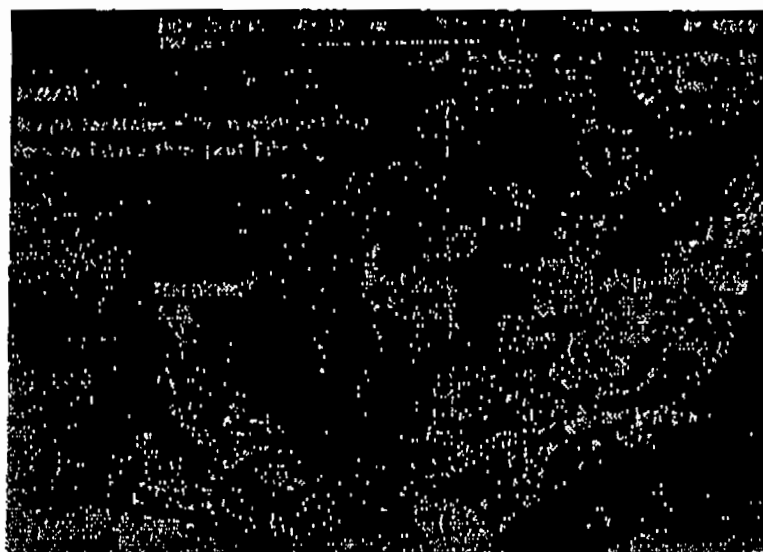


FIG. 15h

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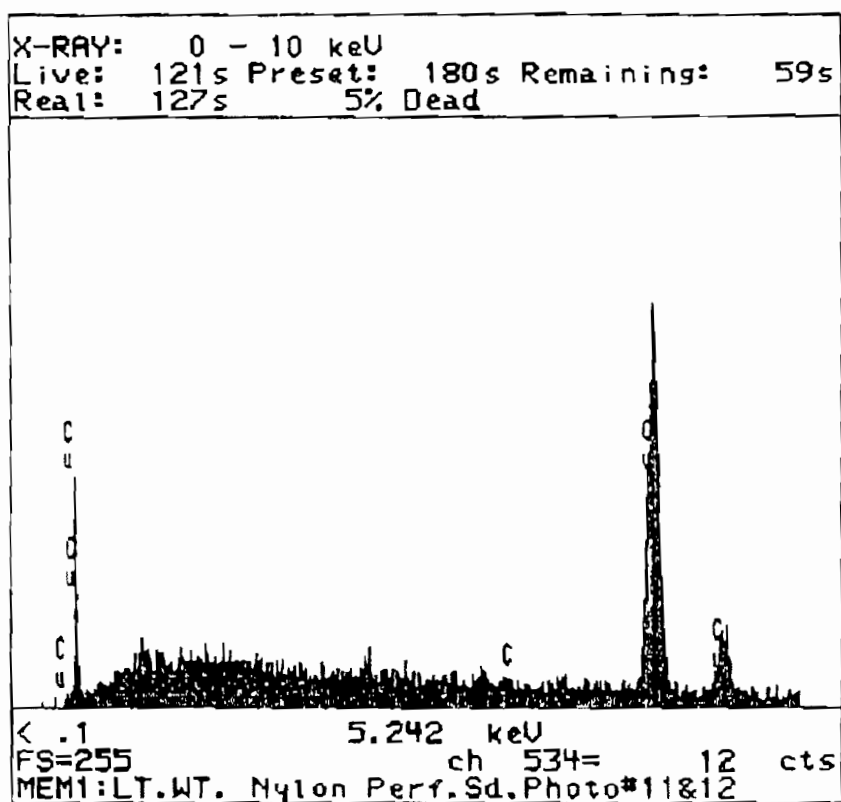


FIG. 15i

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POROUS WEBS HAVING A POLYMER COMPOSITION CONTROLLABLY PLACED THEREIN

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

This application is a division of U.S. patent application Ser. No. 08/407,191 filed on Mar. 17, 1995, U.S. Pat. No. 5,876,792, which is a continuation-in-part of U.S. patent application Ser. No. 08/017,855 filed on Feb. 16, 1993, now U.S. Pat. No. 5,418,051 issued May 23, 1995; which is a continuation of U.S. patent application Ser. No. 07/680,645 filed on Apr. 2, 1991, now U.S. Pat. No. 5,209,965 issued May 11, 1993; which is a continuation of U.S. patent application Ser. No. 07/319,778 filed on Mar. 10, 1989, now U.S. Pat. No. 5,004,643, issued Apr. 2, 1991 which is a continuation-in-part of U.S. patent application Ser. No. 07/167,630 filed on Mar. 14, 1988, now abandoned; which is a continuation-in-part of Ser. No. 07/167,643 filed on Mar. 14, 1988, now abandoned; which is a continuation-in-part of Ser. No. 07/167,797 filed on Mar. 14, 1988, now abandoned; which is a continuation-in-part of Ser. No. 07/167,869 filed on Mar. 14, 1988, now abandoned; all of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods of and apparatus for the introduction of sufficient energy to controllably and selectively place a polymer composition into a porous web. The present invention more particularly relates to methods of and apparatus for the controlled placement of a curable, shear thinning, polymer composition into a web. The controlled placement is preferably performed through the energy controlled viscosity and rheology modified placement of the polymer composition by 1) applying the polymer composition onto a surface of a web, 2) shear thinning the composition and placing it into the web, and 3) curing the polymer composition. This method and apparatus produces a web that either has some of its fibers or structural elements encapsulated by the polymer composition while at least some of the interstitial spaces of the web are open; or has an internal layer extending through the web in a direction generally spaced from at least one major surface thereof; or has both encapsulated structural elements and an internal layer of polymer composition.

2. Description of Related Art

In the prior art, it has been proposed to treat porous webs, especially fabrics, with silicone resins and also with fluorochemicals. Conventional treatments of webs fall into the general categories of (i) surface coatings and (ii) saturations or impregnations.

For example, U.S. Pat. Nos. 3,436,366; 3,639,155; 4,472,470; 4,500,584, and 4,666,765 disclose silicone coated fabrics. Silicone coatings are known to exhibit relative inertness to extreme temperatures of both heat and cold and to be relatively resistant to ozone and ultraviolet light. Also, a silicone coating can selectively exhibit strength enhancement, flame retardancy and/or resistance to soiling. Fluorochemical treatment of webs is known to impart properties, such as soil resistance, grease resistance, and the like.

Prior art fluorochemical and silicone fabric treatment evidently can protect only that side of the fabric upon which they are disposed. Such treatments significantly alter the

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hand, or tactile feel, of the treated side. Prior silicone fabric coatings typically degrade the tactile finish, or hand, of the fabric and give the coated fabric side a rubberized finish which is not appealing for many fabric uses, particularly garments.

U.S. Pat. No. 4,454,191 describes a waterproof and moisture-conducting fabric coated with a hydrophilic polymer. The polymer is a compressed foam of an acrylic resin modified with polyvinyl chloride or polyurethane and serves as a sort of "sponge", soaking up excess moisture vapor. Other microporous polymeric coatings have been used in prior art attempts to make a garment breathable, yet waterproof.

Various polyorganosiloxane compositions are taught in the prior art that can be used for making coatings that impart water-repellency to fabrics. Typical of such teachings is the process described in U.S. Pat. No. 4,370,365 which describes a water repellent agent comprising, in addition to an organohydrogenpolysiloxane, either one or a combination of linear organopolysiloxanes containing alkene groups, and a resinous organopolysiloxane containing tetrafunctional and monofunctional siloxane units. The resultant mixture is catalyzed for curing and dispersed into an aqueous emulsion. The fabric is dipped in the emulsion and heated. The resultant product is said to have a good "hand" and to possess waterproofness.

This type of treatment for rendering fabrics water repellent without affecting their "feel" is common and well known in the art. However, it has not been shown that polyorganosiloxanes have been coated on fabrics in such a way that both high levels of resistance to water by the fibers/filaments and high levels of permeability to water vapor are achieved. As used herein, the term "high levels of permeability to water vapor" has reference to a value of at least about 500 gms/m²/day, as measured by ASTM E96-80B. Also, as used herein, the term "high level of waterproofness" is defined by selective testing methodologies discussed later in this specification. These methodologies particularly deal with water resistance of fabrics and their component fibers.

Porous webs have been further shown to be surface coated in, for example, U.S. Pat. Nos. 4,478,895; 4,112,179; 4,297,265; 2,893,962; 4,504,549; 3,360,394; 4,293,611; 4,472,470; and 4,666,765. These surface coatings impart various characteristics to the surface of a web, but do not substantially impregnate the web fibers. Such coatings remain on the surface and do not provide a film over the individual internal fibers and/or yarn bundles of the web. In addition, such coatings on the web surface tend to wash away quickly.

Prior art treatments of webs by saturation or impregnation also suffer from limitations. Saturation, such as accomplished by padbath immersion, or the like, is capable of producing variable concentrations of a given saturant chemical.

To treat a flexible web, by heavy saturation or impregnation with a polymer material, such as a silicone resin, the prior art has suggested immersion of the flexible web, or fabric, in a padbath, or the like, using a low viscosity liquid silicone resin so that the low viscosity liquid can flow readily into, and be adsorbed or absorbed therewithin. The silicone resin treated product is typically a rubberized web, or fabric, that is very heavily impregnated with silicone. Such a treated web is substantially devoid of its original tactile and visual properties, and instead has the characteristic rubbery properties of a cured silicone polymer.

U.S. Pat. No. 2,673,823 teaches impregnating a polymer into the interstices of a fabric and thus fully filling the

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interstices. This patent provides no control of the saturation of the fabric. It teaches full saturation of the interstices of the fabric.

The prior art application of liquid or paste compositions to textiles for purposes of saturation and/or impregnation is typically accomplished by an immersion process. Particularly for flexible webs, including fabric, an immersion application of a liquid or paste composition to the web is achieved, for example, by the so-called padding process wherein a fabric material is passed first through a bath and subsequently through squeeze rollers in the process sometimes called single-dip, single-nip padding. Alternatively, for example, the fabric can be passed between squeeze rollers, the bottom one of which carries the liquid or paste composition in a process sometimes called double-dip or double-nip padding.

Prior art treatment of webs that force a composition into the spaces of the web while maintaining some breathability have relied on using low viscosity compositions or solvents to aid in the flow of the composition. U.S. Pat. No. 3,594,213 describes a process for impregnating or coating fabrics with liquified compositions to create a breathable fabric. This patent imparts no energy into the composition to liquify it while forcing it into the spaces of the web. The composition is substantially liquified before placement onto and into the web. U.S. Pat. No. 4,588,614 teaches a method for incorporating an active agent into a porous substrate. This patent utilizes a solvent to aid in the incorporation of the active agent into the web.

Prior art apparatus for the coating of webs, including fabrics, generally deposits a coating onto the fabric at a desired thickness. Coating at a predetermined thickness can be achieved by deposition of coating material or by the scraping of a coating upon the fabric by knives. Flexible webs are generally urged between oppositely disposed surfaces, one of which would be a doctoring blade or drag knife. The blade or knife smooths the coating and maintains the thickness of the coating to a desired thickness. For example, it is possible to apply a relatively thick silicone liquid elastomer coating to a rough web, typically of fiberglass, in order to make architectural fabric as is taught in U.S. Pat. No. 4,666,765. In this example, the drag knives are set to a thickness of about 2 to 10 mils thicker than the web thickness. This setting, depending on the coating speed, can yield a base coat thickness of approximately 3 to 12 mils thicker than the web thickness.

Various types of coatings, and various coating thicknesses, are possible. However, a general principle of coating machinery is that the coating material is swept, or dragged, along the surface of the fabric. No special attention is normally given to any pressured forcing of the coating into the fabric, therein making the coating also serve as an impregnant. Of course, some coating will be urged into surface regions of the fabric by the coating process. Generally, however, application of high transversely exerted (against a fiber or web surface) forces at the location of the coating deposition and/or smoothing is not desired in the prior art processes because it is the goal of the prior art coating processes to leave a definite thickness of coating material upon a surface of the fabric, and not to scrape the fabric clean of surface-located coating material.

One prior art silicone resin composition is taught by U.S. Pat. Nos. 4,472,470 and 4,500,584, and includes a vinyl terminated polysiloxane, typically one having a viscosity of up to about 2,000,000 centipoises at 25° C., and a resinous organosiloxane polymer. The composition further includes a

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platinum catalyst, and an organohydrogenpolyloxane crosslinking agent, and is typically liquid. Such composition is curable at temperatures ranging from room temperature to 1100° C. or higher depending upon such variables as the amount of platinum catalyst present in the composition, and the time and the temperature allowed for curing.

Such compositions may additionally include fillers, including finely divided inorganic fillers. Silicone resin compositions that are free of any fillers are generally transparent or translucent, whereas silicone resin compositions containing fillers are translucent or opaque depending upon the particular filler employed. Cured silicone resin compositions are variously more resinous, or hard, dependent upon such variables as the ratio of resinous copolymer to vinyl terminated polysiloxane, the viscosity of the polysiloxane, and the like.

Curing (including polymerization and controlled crosslinking) can encompass the same reactions. However, in the fabric finishing arts, such terms can be used to identify different phenomena. Thus, controllable and controlled curing, which is taught by the prior art, may not be the same as control of crosslinking. In the fabric finishing arts, curing is a process by which resins or plastics are set in or on textile materials, usually by heating. Controlled crosslinking may be considered to be a separate chemical reaction from curing in the fabric finishing arts. Controlled crosslinking can occur between substances that are already cured. Controlled crosslinking can stabilize fibers, such as cellulosic fibers through chemical reaction with certain compounds applied thereto. Controlled crosslinking can improve mechanical factors such as wrinkle performance and can significantly improve and control the hand and drape of the web. Polymerization can refer to polymer formation or polymer growth.

SUMMARY OF THE INVENTION

The present invention includes methods and apparatus for controlling a porous web under tension, for applying a curable or semi-curable, shear thinnable polymer composition onto the surface of the web, for shear thinning the polymer composition, and placing it into the web to position the polymer within the web in a certain manner, and for partially or fully curing the polymer composition. The methods and apparatus of this invention control the placement of the composition into the web to either encapsulate the structural elements (i.e., the fibers or filaments) making up the web leaving at least some of the interstitial spaces open or providing an internal layer of polymer between the upper and lower surfaces of the web, or some combination of the foregoing.

The methods and apparatus of the present invention permits the application of the polymeric composition onto the surface of the web by a variety of means. After the polymer is applied to the surface of the web, the polymer composition is preferably immediately shear thinned to controllably and significantly reduce its viscosity and place it into selected places within the web. To aid in this process, the web is preferably distorted, typically by stretching at the location of the shear thinning. This distortion facilitates the entrance of the polymer composition into the web by creating a double or dual shear thinning. In the case of the web, this is produced by the combination of the edge condition of the blade, the engineered shear thinnable polymer, the speed of the web, and the subsequent repositioning of the fibers and filaments after their immediate passage under the edge of the blade.

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Controlled placement of the polymer composition within a web may be performed by a basic embodiment of a machine in accordance with the present invention, that is as simple as an applicator to apply viscous polymer to the surface of the web, a pair of facilities for applying tension to a section of the web and a blade forced against the web in the section under tension. The web is pulled under tension past the blade, or, alternatively, the blade is moved relative to the web, and the forces generated by the blade cause the polymer composition to flow into the three-dimensional matrix of the web, and controllably be extracted out of the web leaving a thin film of polymer encapsulating selected fibers, or an internal layer of polymer, or both. Tension on the web is preferably released thereafter, and the web is cured.

The present invention includes novel methods and apparatus for manufacturing webs, fibers and fabrics that have certain desirable physical qualities such as water resistance, increased durability, and improved barrier qualities by combining the use of encapsulated fibers and filaments and a breathable or controlled pore size internal coating with a controlled surface chemistry modification and the like. Such webs, fibers and fabrics can be used to prepare a wide variety of products including, but not limited to, carpets, specialized clothing, career apparel, bioengineered surfaces for diagnostic applications, and upholstery. By use of the present invention, webs, fibers and fabrics can be manufactured with a wide variety of desired physical characteristics.

Methods and apparatus of the present invention can treat webs or fabrics which are generally flat or planar with great internal precision of the internal placement, by combining the use of encapsulated fibers and filaments and a breathable or controlled pore size internal layer, with a controlled surface chemistry modification. Surface chemistry is controlled by using sufficient web tension and frontal blade energy to dislodge the fluorocarbon from the web which is then caused to surface orient and/or bloom. The webs or fabrics can comprise fibers in the form of monofilaments, yarns, staples, or the like. The webs or fabrics can also be comprised of a matrix having open cells or pores therein. The webs or fabrics may be a fabric which is woven or non-woven with fibers that can be of any desired composition. The webs or fabrics will generally be tensionable, but not too weak or elastomeric to be processed in accordance with the teachings of the present invention. Any web that is too weak or elastomeric can be treated in accordance with the subject invention if it is laminated to a support backing of paper, film, such as Mylar, or the like and controllably stretched or not stretched prior to applying the backing, thereby setting the condition under which it is stabilized so that it can be treated in accordance with this invention.

The methods and apparatus of this invention are also applicable to treating discrete sheets or pieces of webs such as papers, film sheets, foam sheets, leather hides, woven and non-woven sheets, and the like. The sheet is fed into the apparatus and stops. It is placed under tension and polymer is applied. Rigid or non-rigid blades are moved across the surface of the sheet to cause the controlled placement of the polymer within the sheet as previously described. A non-rigid blade can be flexible but must have sufficient shearing capability.

Webs treated by the methods and apparatus of the present invention contain a curable or semi-curable polymer or copolymer that may contain monomers that are present as a film, coating, or layer within a web that envelopes or encapsulates at least a portion of the fibers or cell or pore walls of the web. The internal layer is a region generally

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spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymers controllably placed therein and the fibers and filaments of the web in this region. The interstices or open cells in the region of the internal layer are also substantially filled. The outer surfaces of the web are substantially free of any polymer deposits other than the thin film encapsulation of the surface fibers and filaments. However, the web remains breathable and is either water resistant or waterproof. The thickness of the internal layer is generally in the range of 0.01 to 50 microns.

At a microscopic level, a web treated in accordance with the present invention, for example, a fabric, can be regarded as being a complex structure, but generally the internal layer is discernable under microscopic examination as shown in the accompanying scanning electron microscope photographs that will be discussed hereinafter.

Depending upon the conditions used to produce it, a web produced in accordance with the present invention can characteristically and preferably exhibit a soft hand and flexibility that is comparable to the hand and flexibility of the untreated web. In some cases, the difference between the hand and the feel of the treated and untreated webs may not be perceptible, but may be engineered to be altered through the controlled crosslinking of the polymer. This is particularly surprising in view of the substantial amount of polymer being added to the web. A treated web has a breathability which, by a present preference, can approach a high percentage of the untreated web notwithstanding the relatively large amount of polymer present.

A polymer composition having a viscosity in the range of greater than 1,000 centipoise but less than 2,000,000 centipoise is preferably used to produce the treated webs. If desired, additives or modifiers can be admixed with such a composition to adjust and improve properties of such composition or web, such as viscosity and/or rheology, combustibility, reflectivity, flexibility, conductivity, light fastness, mildew resistance, rot resistance, stain resistance, grease resistance, and the like. In general, a web treated in accordance with this invention exhibits enhanced durability. These additives are generally controlled by the engineered shear thinning polymer composition and the method and apparatus of this invention to be oriented and surface exposed on the surface of the thin film on the encapsulated fibers, or on one or both surfaces of the internal layer, or on one or both surfaces of the web, or some combination of the above.

A web made by the present invention can preserve much, or even substantially all, of its original untreated hand even after an extended period of use while demonstrating excellent abrasion resistance. In contrast, an untreated web typically loses its original hand and displays reduced abrasion resistance after an extended period of use. This is achieved by the formation of an internal layer that prevents new fiber surfaces from being exposed, thereby minimizing the amount of untreated surfaces that degrade much faster than the treated fibers.

A web treated by this invention can undergo a large number of machine washings with detergent without experiencing appreciable or significant change or deterioration. The polymer matrix composition prolongs the use and service life of a web, usually by at least an order of magnitude, depending on such factors as web type, extent and type of treatment by the teachings of this invention, and the like.

Optionally, and as indicated above, agents or additives carried by the polymer composition into a web can be stably

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fixed and selectively placed in the web with the cured polymer. For example, agents such as ultraviolet light absorbers, dulling agents, reflectivity enhancers, antimicrobial agents, flame resistant agents, heat absorbant, anti-static agents, and the like, which modify a web's response to light and radiation are desirably located substantially upon the surfaces of the web's fibers. When these agents are incorporated into the enveloping polymer film, it appears that they are retained where they are deposited. A present preference for ultraviolet resistant webs in the practice of this invention is to employ a silicone polymer composition that contains a benzophenone.

In addition, the present invention is directed to methods and apparatus for making polymer encapsulated and internally coated webs. Such methods and apparatus includes means for tensioning a porous, flexible web; means for applying a curable, shear thinnable, polymer composition thereto; and means for applying a localized shear force sufficient to cause the controlled shear thinning of an engineered polymer over and against one or both surfaces of the tensioned web. The shear force is sufficient to shear thin the polymer, to selectively disintegrate and place the polymer composition within the web as an internal layer in a region extending generally in spaced relationship to the surfaces of the web and to generally envelop surface portions of at least some of the web fibers or form a lining of the cells or pores of the web. The internal layer is not necessarily flat but may undulate or meander through the web, occasionally even touching one or both surfaces of the web. Alternatively, the shear force and other variables are controlled to encapsulate at least some of the internal and external fibers of the web without forming an internal layer. Also, control of the methods and apparatus can result in a treated web having a combination of an internal layer and encapsulation of at least some of the fibers of the web leaving at least some of the interstitial spaces open. The web is then optionally intertemporarily stored, or is (preferably) immediately subjected to curing conditions (heat, moisture and/or radiation) which converts the polymer composition as deposited in the web into a solid elastomeric polymer. The web can be semi-cured or partially cured and can be finally cured or post cured at a later time.

Various other and further features, embodiments, and the like which are associated with the present invention will become apparent and better understood to those skilled in the art from the present description considered in conjunction with the accompanying drawings wherein presently preferred embodiments of the invention are illustrated by way of example. It is to be expressly understood, however, that the drawings and the associated accompanying portions of this specification are provided for purposes of illustration and description only, and are not intended as limitations on the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical plot illustrating the flow of a silicone polymer composition over time upon and in fabrics both pretreated and untreated with water repellent chemicals, such as fluorocarbons.

FIG. 2 is a plan view of a prior art silicone polymer treated fabric magnified 150 times.

FIG. 3a is a photomicrograph of a fabric of the invention magnified 120 times.

FIG. 3b is a cross section of a fiber bundle fabric of FIG. 3a magnified 600 times.

FIG. 3c is a view of the side of the fabric of FIG. 3a that is the opposite of the side to which silicone polymer was applied.

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FIGS. 4a and 4b illustrate diagrammatically one embodiment of a method and apparatus suitable for use in the practice of the present invention.

FIG. 5 is a diagrammatic representation illustrating the process in accordance with the present invention.

FIG. 6 illustrates diagrammatically another embodiment of a method and apparatus suitable for use in the practice of the present invention.

FIG. 7 illustrates diagrammatically another embodiment of a method and apparatus suitable for use in the practice of the present invention.

FIGS. 8a through 8d are graphs illustrating ways of plotting rheological behavior.

FIG. 9 is a schematic vector diagram illustrating surface tension forces.

FIG. 10 is a graph relating contact angle over a smooth, solid surface.

FIGS. 11a through 11d show representative velocity profiles.

FIGS. 12a through 12c illustrate diagrammatically other methods and apparatus suitable for use in the practice of the present invention.

FIGS. 13a through 13c are scanning electron microscope photomicrographs of another representative fabric made in accordance with of the present invention.

FIG. 14 illustrates diagrammatically another and presently preferred embodiment of methods and apparatus suitable for use in the practice of the present invention.

FIGS. 15a through 15f are scanning electron microscopy (SEM) photomicrographs and elemental analyses which depict various results in fabrics, fibers and filaments from back scatter evaluation tests.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following description is of the best presently contemplated mode of carrying out the invention. This description is made for the purpose of illustrating the general principles of the inventions and should not be taken in a limiting sense.

The present invention relates to methods and apparatus for manufacturing a treated web. The subject methods and apparatus involve the control of numerous variables, including, without limitation, web tension (both overall web tension as well as the web tension immediately before and after each individual blade), angle of entry of web into each blade, blade angle in relation to horizontal reference point, blade pressure against moving web, angle of exit of web from each blade, web speed, number of blades, the pressure of the leading nip rolls, the pressure of the trailing nip rolls, static control, thickness of each blade, bevel on each blade, oven cure temperature, oven cure dwell time, blade temperature and blade surfaces and edge conditions and blade finish.

Other variables that affect the finished product, but are not directly related to the methods and apparatus, include, without limitation, the polymer blend, the starting viscosity of the polymer composition, accelerators added to the polymer composition, additives added to the polymer composition, the type of web used, ambient temperature, humidity, airborne contaminants, lint on web, pre-treatment of web, sub-web surface temperature, and web moisture content.

With respect to the blades, the temperature of the blade can be kept cool to keep the polymer composition from

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curing prematurely. This can be accomplished by passing a coolant through or around the blade or by other means well known in the art. Alternatively, the blade could be heated by passing a heated fluid around or through the blade, if desired to improve or alter the viscosity and rheology for the required changes in the polymer necessary to achieve a specific product.

The blade finish is also important. A hard, smooth surface of both blade face and edges is desirable to shear thin the polymer and keep it flowing and to maximize friction or selectively create shear forces between the web, the polymer, and blade(s). For some applications, the blades should preferably remain rigid in all dimensions and have minimal resonance in order to get uniform web treatment.

The apparatus has facilities for rotating the angle of each blade $\pm 90^\circ$ from the vertical. In order to vary the shear and placement forces of the blade against the web, polymer and additives, adjustment facilities are provided for moving the blade vertically up and down and moving the blade forward and backward horizontally. All three axes are important for creating the desired control which causes the encapsulated fibers and/or filaments, the additive placement and orientation on the fiber and filaments, the optional internal layer, and the controlled thickness of the encapsulating films or internal layer. The lateral placement of each blade relative to the other is also important and facilities are provided for allowing lateral movement of each blade toward and away from each other. The lateral placement of each blade controls the micro tension and elastic vibration of the web between the preceding roll and the blade, thereby controlling the web after the immediate exit of the web from the blade and controlling the Coanda Effect, as described in U.S. Pat. No. 4,539,930, so that controlled placement of the internal layer takes place.

Changing the tension of the web results in changes internally in the web, such as the position of the internal layer of the web, as well as how much or how little fiber encapsulation occurs, and the thickness of the film encapsulating the individual fibers or filaments.

At the leading edge of the blade, the web is stretched longitudinally and the polymer is simultaneously and dynamically shear thinned, placed into the web, and partially extracted from the web, thereby leaving encapsulated fibers and filaments and/or an internal layer. As the web passes the leading edge of the blade, the elastic recovery forces of the web combined with the relaxation or elastic recovery of the fibers and filaments causes fiber encapsulation and the surface chemistry modification (or bloom). It is believed that this occurs by the popping apart of the individual fibers and filaments. The fibers and filaments either pull the polymer from the interstitial spaces or the rheology of the polymer attracts it to the fibers and filaments or some combination of the two. The end result is that the polymer in the interstitial spaces moves to the fibers and filaments as they move or snap apart, thereby creating encapsulated fibers and filaments. At the bottom surface of the blade, the thickness, depth, and controlled placement of the internal layer is determined. A wider blade results in a thicker internal layer of polymer. Further, the dynamics of stretch and relaxation of the fibers provides for an even energy necessary for the thin film encapsulation of the polymer composition over the fibers.

Passing the treated web through the exit nip rolls pushes the fibers or structural elements of the web together. The hardness of and the material of the exit nip rolls affects the finished web. The exit nip rolls could be either two rubber

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rolls or two steel rolls, or one steel roll and one rubber roll, and the rubber rolls could be of different durometers. Further, the variation of the hardness of one or both nip rolls changes the contact area or footprint between the nip rolls and the web as the web passes therebetween. With a softer roll there is a larger contact area and the web is capable of retaining the (a) thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) controlled placement of the additives in (a) and (b). With a harder roll there is a smaller contact area which is appropriate for heavier webs.

Additional controllable variables include the various controls of each blade, the nip rolls durometer, the nip release effect, the nip surface characteristics, the guidance, and the pre-treatment of the substrate. Some of the controllable variables are: 1) web tension, 2) angle of entry of fabric into the blade, 3) blade angle in reference to horizontal position, 4) blade pressure against fabric (blade height), 5) angle of exit of fabric from blade, 6) web speed, 7) number of blades, 8) initial rheology and viscosity of polymers, 9) nip pressure, 10) entry nip pressure, 11) static control, 12) blade thickness and shape, 13) polymers and polymer blends, 14) accelerators and inhibitors added to polymers, 15) additives in polymers, 16) oven cure temperature, 17) oven cure dwell time, 18) substrate type, 19) ambient polymer temperature, 20) humidity, 21) degree web is deformed under lateral tension, and 22) airborne contaminants and lint on the web. Control of the above variables affects: (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b).

An increase in web tension causes less polymer to be applied to the web, and also, more of what is applied to be extracted from the web. Web tension occurs between the entrance pull stand and the exit pull stand. The primary tension is a result of the differential rate between the driven entrance pull stand and the driven exit pull stand whereby the exit pull stand is driven at a rate faster than the entrance pull stand. Other factors which effect tension are (1) the blade roll diameter, (2) the vertical depth of the blade(s), (3) the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, and (4) the friction as the web passes under the blade(s). The larger the blade roll diameter, the higher the tension of the web. If the drive rate of the web remains constant, then increasing the depth of the blade into the web creates a greater micro tension condition under the blade. Similarly, decreasing the depth into the web decreases the micro tension under the blade. The lower the durometer of the entrance pull stand roll and rubber roll of the exit pull stand, the larger the footprint or contact area between the rolls. A larger footprint produces more surface friction, thereby limiting web slippage and increasing tension. Likewise, web slippage can be effected by changing the surface texture of the rolls, i.e., a smooth roll will allow greater slippage than a highly contrasting or rough surface texture. Increasing friction, as the fabric passes under the blade(s), also produces tension. Friction is a function of the surface area of the bottom of the blade(s). Increasing the surface area increases the friction which increases the tension.

The entry angle of the web into the blade(s) can be varied by blade roll height, blade roll diameter, blade angle, distance between prior blade roll(s) and blade(s), and height of the blades. Increasing the blade roll height and blade roll diameter increases the entry angle into the blade. Rotating the blade angle clockwise from the perpendicular, with the web running left to right, increases the entry angle.

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Likewise, rotating the blade angle counter-clockwise from the perpendicular, with the web running left to right, decreases the entry angle. Decreasing the distance between the roll before the blade and the blade decreases the angle of entry. Increasing the downward depth of the blade(s) into the web decreases the angle of entry into the blade(s).

The angle of the blade(s) is completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel shape, resonance, texture, or material can be mounted. Ideally the apparatus contains two or three blades per blade mount.

The blade height or blade pressure applied against a web can be obtained through the vertical positioning of the blade(s) in the blade mount. The greater the downward depth of the blade(s), the greater the pressure. Blade pressure against the web is also accomplished through the tension of the web as described above.

The same line components that affect the entry angle of the web into the blade(s), also affect the exit angle of the web out of the blade. Any changes in blade roll(s) vertical height, diameter, or distance away from the blade, affects the exit angle of the web. If the angle of the blade is rotated clockwise as described above, the entry angle of the web increases, thus decreasing the exit angle.

Web speed is proportional to the variable speed of the motor which drives the entrance and exit nip stands. Web speed can effect the physics of the polymers as the web passes under the blades.

The number of blades can vary. Generally, more than one blade is required. The polymer is first applied onto the web prior to the first blade. At this blade, a rolling bead of polymer can exist at the interface of the blade and the web (entry angle). Basically, a high viscosity polymer is applied and through the process of shear thinning, the viscosity is greatly decreased, allowing the polymer to enter into the interstitial spaces of the web. Any blade(s) after the first blade, serves to further control the polymer rheology and viscosity and continue the controlled placement of the polymer into the web. This is accomplished by controllably removing excess polymer to obtain an even distribution of polymer to any area, or a combination of the three areas of a) the thin film encapsulation of the individual fibers and filaments, b) the controlled placement of the internal layer, and c) the controlled placement of the additives in a) and b).

The initial process dynamics for the rheology and viscosity of the polymer is designed and engineered with the required attributes to achieve (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal layer, and (c) the controlled placement of the additives in (a) and (b). If the polymer viscosity is high, the polymer may need to be pre-thinned by using a dynamic mixer or three-roll head, as shown in FIG. 12a. The dynamic mixer or the three-roll head can significantly reduce the viscosity and even pre-place the polymer into a thick substrate or web to allow the blades to further shear thin and enhance the flow and placement of the polymer.

The entrance pull stand is a driven roll proportionally driven at a predetermined rate slower than the exit pull stand. The entrance and exit pull stands are adjustable from about 100 pounds of force to 5 or more tons of force.

The bottom rolls of both the entrance and exit pull stands have micro-positioning capability to provide for gap adjustment and alignment. The composition of the top roll of the

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entrance and exit pull stands is chosen based on the durometer of the urethane or rubber. The top roll of the exit pull stand preferably utilizes a Teflon sleeve which will not react with the polymers used in the process. The bottom roll of the exit pull stand is preferably chrome plated or highly polished steel to reduce the impression into the preplaced polymer in the web.

If desired, non-contact antistatic devices may be installed in locations where noticeable levels of static buildup are detected. However, there is no evidence of adverse effects due to static buildup in the process.

Blade thickness and shape have substantial effects on the movement of the structural elements of the web during processing and more importantly, the viscoelastic flow characteristics of the polymer in controlling (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b). The blade bevel can effect the entry angle of the web and effect the sharpness of the leading edge of the blade. A sharper leading edge has a greater ability to push the weave or structural elements of the web longitudinally and transversely, increasing the size of the interstitial spaces. As the web passes the leading edge of the blade, the interstitial spaces snap back or contract to their original size. The polymer viscosity is reduced and the polymer is placed into the web at the leading edge of the blade. Blade thickness and shape effects the polymers and their selected additives and the placement thereof. Preferably, the combination of the leading edge condition and the two surfaces (the front and the bottom) that meet at the leading edge are RMS 5 or better in grind and/or polish. This creates a precise leading edge; the more precise the leading edge, the more the shear thinning control.

There are a number of pre-qualifiers or engineered attributes of polymers that enhance control of flow and polymer placement in: (a) the thin film encapsulation of the individual fibers and filaments, (b) the controlled placement of the internal coating, and (c) the controlled placement of the additives in (a) and (b). Blending polymers is one way to achieve ideal flow and placement characteristics. An example of a blended polymer is where one polymer, selected for its physical properties, is mixed with another polymer that is selected for its viscosity altering properties. Many tests using different polymer blends have been done. Polymer blends vary by both chemical and physical adhesion, durability, cure dwell time required, cure temperature required, flexibility, percentage add-on required, performance requirements, and aesthetics.

Accelerators and inhibitors which are added to polymers, generally produce three effects. An illustrative accelerator or inhibitor is a platinum catalyst, which is a cure or crosslinking enhancer. The first effect it produces is to control the time and temperature of the web as it cures. A cure or controlled crosslinking enhancer can significantly assist in controlling the drape and hand feel of the web. The second effect is to alter the cure to allow the web to reach partial cure and continue curing after leaving an initial heat zone. This second effect also assists in retaining the drape and hand feel of the web. The third effect of inhibitors is to achieve a semi-cure for later staging of the cure.

Additives which are added to the polymers significantly control surface chemistry. Surface chemistry characteristics are controlled by including additives that have both reactive and bio-interactive capabilities. The method and apparatus of this invention can control the placement of the additives

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on the surface of the thin film encapsulating the fibers, on either or both surfaces of the internal layer, on either or both surfaces of the web, or any combination of the foregoing.

The oven cure temperature and the source and type of cure energy, are controlled for a number of reasons. The oven cure temperature is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure temperature is thermostatically controlled to a predetermined temperature for the web and polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, aesthetics, etc. The effect on the web depends on the oven temperature, dwell time and curing rate of the polymer. Webs may expand slightly from the heat.

Oven cure dwell time is the duration of the web in the oven. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

The physical construction and chemistry of the web is critical. The amount of control over the rheology of the polymer and the tension on the web are dependent on the physical construction and chemistry. The web selected must have physical characteristics that are compatible with the flow characteristics of the polymer.

The ambient polymer temperature refers to the starting or first staging point to controlling the viscosity and rheology. The process head can control the ambient polymer temperature through temperature controlled polymer delivery and controlled blade temperatures.

Humidity can sometimes inhibit or accelerate curing of the polymer. Therefore, humidity needs to be monitored and, in some conditions, controlled.

The degree the web is deformed under lateral tension is controllable by the choice of the physical construct of the web, the blade angle, the blade loading edge condition, and the micro and macro tension of the web.

Airborne contaminants and lint on the web can affect primability and can create pin holes in the polymer. Therefore, airborne contaminants and lint on the web need to be controlled to reduce or eliminate pin holes or uncontrolled primability.

In view of the fact that between the shear thinning stations and the oven, the polymer composition may begin to set or partially cure, it may be desirable to overshear so that by the time the web gets to the curing oven, it will be at the point where it is desired that the cure occur. This over shear effect is a matter of controlling certain variables, including the force of the blades against the moving web, as well as the tension and speed of the web.

By having a number of shear thinning blades, you create a multiple shear thinning effect, which changes the final construct of the polymer and the (a) thin film encapsulation of the individual fibers and filaments, (b) controlled placement of the internal coating, and (c) controlled placement of the additives in (a) and (b). It is understood that the first shear thinning causes viscoelastic deformation of the poly-

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mer composition which, due to its memory, tends to return to a certain level. With each multiple shear thinning, the level to which the polymer starts at that shear point and returns is changed. This is called thixotropic looping or plateauing.

Definitions

The term "web" as used herein is intended to include fabrics and refers to a sheet-like structure (woven or non-woven) comprised of fibers or structural elements. Included with the fibers can be non-fibrous elements, such as particulate fillers, binders, dyes, sizes and the like in amounts that do not substantially affect the porosity or flexibility of the web. While preferably, at least 50 weight percent of a web treated in accordance with the present invention is fibers, more preferred webs have at least about 85 weight percent of their structure as fiber. It is presently preferred that webs be untreated with any sizing agent, coating, or the like, except as taught herein. The web may comprise a laminated film or fabric and a woven or non-woven porous substrate. The web may also be a composite film or a film laminated to a porous substrate or a double layer.

The term "webs" includes flexible and non-flexible porous webs. Webs usable in the practice of this invention can be classified into two general types:

(A) Fibrous webs; and

(B) Substrates having open cells or pores, such as foams.

A porous, flexible fibrous web is comprised of a plurality of associated or interengaged fibers or structural elements having interstices or interstitial spaces defined therebetween. Preferred fibrous webs can include woven or non-woven fabrics. Other substrates include, but are not limited to, a matrix having open cells or pores therein such as foams or synthetic leathers.

The term "fiber", as used herein, refers to a long, pliable, cohesive, natural or man-made (synthetic) threadlike object, such as a monofilament, staple, filament, or the like. A fiber usable in this invention preferably has a length at least 100 times its diameter or width. Fibers can be regarded as being in the form of units which can be formed by known techniques into yarns or the like. Fibers can be formed by known techniques into woven or non-woven webs (especially fabrics) including weaving, knitting, braiding, felt, twisting, matting, needling, pressing, and the like. Preferably, fibers, such as those used for spinning, as into a yarn, or the like, have a length of at least about 5 millimeters. Fibers such as those derived from celluloses of the type produced in paper manufacture can be used in combination with longer fibers as above indicated, as those skilled in the art will readily appreciate.

The term "filament" as used herein refers to a fiber of indefinite length.

The term "yarn" as used herein refers to a continuous strand comprised of a multiplicity of fibers, filaments, or the like in a bundled form, such as may be suitable for knitting, weaving or otherwise used to form a fabric. Yarn can be made from a number of fibers that are twisted together (spun yarn) or a number of filaments that are laid together without twist (a zero-twist yarn).

A flexible porous web used as a starting material in the present invention is generally and typically, essentially planar or flat and has generally opposed, parallel facing surfaces. Such a web is a three-dimensional structure comprised of a plurality of fibers with interstices therebetween or a matrix having open cells or pores therein. The matrix can be comprised of polymeric solids including fibrous and non-fibrous elements.

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Non-fibrous elements, such as particulate fillers, binders, dyes, sizes and the like can be added to fibers in a web. Preferred webs have at least about 85% of their structure comprised of fibrous or fiber materials and are untreated with any sizing agent, coating, or the like.

Two principal classes of substrates having open pores or cells may be utilized in the present invention: leathers (including natural leathers, and man-made or synthetic leathers), and foamed plastic sheets (or films) having open cells.

Foamed plastic sheet or film substrates are produced either by compounding a foaming agent additive with resin or by injecting air or a volatile fluid into the still liquid polymer while it is being processed into a sheet or film. A foamed substrate has an internal structure characterized by a network of gas spaces, or cells, that make such foamed substrate less dense than the solid polymer. The foamed sheets or film substrates used as starting materials in the practice of this invention are flexible, open-celled structures.

Natural leathers suitable for use in this invention are typically split hides. Synthetic leathers have wide variations in composition (or structure) and properties, but they look like leather in the goods in which they are used. For purposes of technological description, synthetic leathers can be divided into two general categories: coated fabrics and poromerics.

Synthetic leathers which are poromerics are manufactured so as to resemble leather closely in breathability and moisture vapor permeability, as well as in workability, unactinability, and other properties. The barrier and permeability properties normally are obtained by manufacturing a controlled microporous (open celled) structure.

Synthetic leathers which are coated fabrics, like poromerics, have a balance of physical properties and economic considerations. Usually the coating is either vinyl or urethane. Vinyl coatings can be either solid or expanded vinyl which has internal air bubbles which are usually a closed-cell type of foam. Because such structures usually have a non-porous exterior or front surface or face, such structures display poor breathability and moisture vapor transmission. However, since the interior or back surface or face is porous, such a coated fabric can be used in the practice of this invention by applying the polymer to the back face.

The fibers utilized in a porous flexible web treated by the methods and apparatus of the present invention can be of natural or synthetic origin. Mixtures of natural fibers and synthetic fibers can also be used. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of synthetic fibers include rayon, acetate, polyesters (including polyethyleneterephthalate), polyamides (including nylon), acrylics, olefins, aramids, azlon, glasses, modacrylics, novoloids, nitrils, rayons, sarans, spandex, vinyl, vinyon, regenerated cellulose, cellulose acetates, and the like. Blends of natural and synthetic fibers can also be used.

With respect to the fluorochemical liquid dispersions (or solutions) which can optionally be used for web pretreatment, the term "impregnation" refers to the penetration of such dispersions into a porous web, and to the distribution of such dispersions in a preferably, substantially uniform and controlled manner in such web, particularly as regards the surface portions of the individual web component structural elements and fibers.

With respect to the polymer compositions used in this invention, the term "controlled placement" or "placement" refers to the penetration of such polymer compositions into

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a porous web, to the distribution of such composition in a controlled manner through such web, and to the resultant, at least partial envelopment of at least a portion of the fibers of such web by such composition in accordance with the present invention, or to the formation of an internal layer, or both.

The word "thixotropy" refers herein to liquid flow behavior in which the viscosity of a liquid is reduced by shear agitation or stirring. It is theorized to be caused by the breakdown of some loosely knit structure in the starting liquid that is built up during a period of rest (storage) and that is torn down during a period of suitable applied stress.

The term "coating" as used herein, refers to a generally continuous film or layer formed by a material over or on a surface.

The term "internal coating or internal layer" as used herein, refers to a region spaced from the outer surfaces of the web which is substantially continuously filled by the combination of the polymer controllably placed therein and the fibers and filaments of the web in the specified region. Such coating or layer envelopes, and/or surrounds, and/or encapsulates individual fibers, or lines cell or pore walls of the porous web or substrate, in the specified region. The internal layer is not necessarily flat but may undulate or meander through the web, occasionally even touching one or both surfaces of the web.

The term "envelop" or "encapsulate" as used interchangeably herein, refers to the partial or complete surrounding, encasement, or enclosing by a discrete layer, film, coating, or the like, of exposed surface portions of at least some individual fiber or lining of a cell or pore wall of a porous web. Such a layer can sometimes be contiguous or integral with other portions of the same enveloping material which becomes deposited on internal areas of a web which are adjacent to such enveloping layer, enveloped fiber, lined cell or pore wall, or the like.

The term "elastomeric" as used herein refers to the ability of a cured polymer treated web to stretch and return to its original state.

The term "curing", or "cure", as used herein, refers to a change in state, condition, and/or structure in a material, such as a curable polymer composition that is usually, but not necessarily, induced by at least one applied variable, such as time, temperature, radiation, presence and quantity in such material of a curing catalyst or curing accelerator, or the like. The term "curing" or "cured" covers partial as well as complete curing. In the occurrence of curing in any case, such as the curing of such a polymer composition that has been selectively placed into a porous flexible substrate or web, the components of such a composition may experience occurrence of one or more of complete or partial (a) polymerization, (b) cross-linking, or (c) other reaction, depending upon the nature of the composition being cured, application variables, and presumably other factors. It is to be understood that the present invention includes polymers that are not cured after application or are only partially cured after application.

The term "filled" as used herein in relation to interstices, or interstitial spaces, or open cells, and to the amount of polymer composition therein in a given web, substrate, or the fibers in such web or substrate, designates the presence of such composition therein. When a given interstitial space or open cell is totally taken up by such composition, it is "completely filled" or "plugged". The term "filled" also refers to an interstitial space having a film or layer of polymer composition over or through it so that it is closed even though the entire thickness of the interstitial space is not completely filled or plugged.

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Measurements of the degree of envelopment, interstitial fillage, plugging, or the like in an intercoat coating are conveniently made by microscopy, or preferably by conventional scanning electron microscopy (SEM) techniques. Because of the nature of such measuring by SEM for purposes of the present invention, "a completely filled" interstitial space or open cell can be regarded as a "plugged" interstitial space or open cell.

The term "polymer", or "polymeric" as used herein, refers to monomers and oligomers as well as polymers and polymeric compositions, and mixtures thereof, to the extent that such compositions and mixtures are curable and shear thinnable.

The term "shear thinning", in its broadest sense, means the lowering of the viscosity of a material by the application of energy thereto.

A porous web or fabric is preferably untreated or scoured before being treated in accordance with the present invention. Preferably a web can be preliminarily treated, preferably saturated, for example, by padding, to substantially uniformly impregnate the web with a fluorochemical. Typically, and preferably, the treating composition comprises a dispersion of fluorochemical in a liquid carrier. The liquid carrier is preferably aqueous and can be driven off with heat after application. The treating composition has a low viscosity, typically comparable to the viscosity of water or less. After such a treatment, it is presently preferred that the resulting treated web exhibits a contact angle with water measured on an outer surface of the treated web that is greater than about 90 degrees. The treated web preferably contains fluorochemical substantially uniformly distributed throughout. Thus, the fluorochemical is believed to be located primarily on and in the individual fibers, cells or pores with the web interstices or open cells being substantially free of fluorochemical.

A presently preferred concentration of fluorochemical in a treatment composition is typically in the range of about 1 to about 10% fluorochemical by weight of the total treating composition weight, and more preferably is about 2.5% of an aqueous treating dispersion. Web weight add-ons of the fluorochemical can vary depending upon such factors as the particular web treated, the polymer composition to be utilized in the next step of the treatment process of this invention, the ultimate intended use and properties of the treated web of this invention, and the like. The fluorochemical weight add-on is typically in the range of about 0.01 to about 5% of the weight of the untreated web. After fluorochemical controlled placement, the web is preferably squeezed to remove excess fluorochemical composition after which the web is heated or otherwise dried to evaporate carrier liquid and thereby also accomplish fluorochemical insolubilization or entrenching, if permitted or possible with the particular composition used.

The fluorochemical treated web thereafter has a predetermined amount of a curable polymer composition controllably placed within the web by the methods and apparatus of this invention, to form a web whose fibers, cells or pores are at least partially enveloped or lined with the curable polymer composition, whose web outer surfaces are substantially free of the curable polymer, whose web interstices or open cells are not completely filled with the curable polymer and which may also contain an internal layer of polymer. The curable polymer composition utilized preferably exhibits a viscosity greater than 1,000 centipoise and less than 2,000,000 centipoise at rest at 25° C. at a shear rate of 10 reciprocal seconds.

The fluorochemical residue that remains after web treatment may not be exactly evenly distributed throughout the

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web, but may be present in the web in certain discontinuities. For example, these discontinuities may be randomly distributed in small areas upon an individual fiber's surface. However, the quantity and distribution of fluorochemical through a web is believed to be largely controllable. Some portions of the fluorochemical may become dislodged from the web and migrate through the polymer due to the forces incurred by the shear thinning and controlled placement of the polymer.

The curable polymer composition is believed to be typically polymeric, (usually a mixture of co-curable polymers and oligomers), and to include a catalyst to promote the cure. The polymers that can be used in the present invention may be monomers or partially polymerized polymers commonly known as oligomers, or completely polymerized polymers. The polymer may be curable, partially curable or not curable depending upon the desired physical characteristics of the final product. The polymer composition can include conventional additives.

While silicone is a preferred composition, other polymer compositions can include, polyurethanes, fluorosilicones, silicone-modified polyurethanes, acrylics, polytetrafluoroethylene-containing materials, and the like, either alone or in combination with silicones.

It is to be understood that the depth of polymer placement into a web can be controlled by the methods and apparatus herein described to provide selective placement of the polymer within the substrate or web. The web is thereafter optionally cured to convert the curable composition into a solid elastomeric polymer.

The polymer composition is theorized to be caused to flow and distribute itself over fibers, cells or pores in a web under the influence of the processing conditions and apparatus provided by this invention. This flow and distribution is further theorized to be facilitated and promoted by the presence of a fluorochemical which has been preliminarily impregnated into a web, as taught herein. The amount of fluorochemical or fluorochemical residue in a web is believed to influence the amount, and the locations, where the polymer will collect and deposit, and produce encapsulated fibers and/or an internal layer in the web. However, there is no intent to be bound herein by theory.

Some portion of the residue of fluorochemical resulting from a preliminary web saturating operation is theorized to be present upon a treated fiber's surfaces after envelopment of fibers, cells or pores by the polymer has been achieved during the formation of the encapsulating fiber and/or the internal layer by the practice of this invention. This is believed to be demonstrated by the fact that a web treated by this invention still exhibits an enhanced water and oil repellency, such as is typical of fluorochemicals in porous webs. It is therefore believed that the fluorochemicals are affecting the adherence of the polymer as a thin film enveloping layer about the treated fibers, cells or pores as well as facilitating polymer pressurized flow within and about the interstices or open cells of the web being treated so that the polymer can assume its position enveloping the fibers or lining the cells or pores of the substrate.

In those fabrics that are pretreated with fluorochemicals, the exact interrelationship between the polymer film and the impregnated fluorochemical is presently difficult, or perhaps impossible, to quantify because of the variables involved and because transparent polymer is difficult to observe by optical microscopy. It can be theorized that perhaps the polymer and the fluorochemical each tend to produce discontinuous films upon the fiber surface, and that such films are discontinuous in a complementary manner. It may alter-

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natively be theorized that perhaps the polymer film is contiguous, or substantially so, relative to fluorochemical molecules on a fiber surface, and that the layer of polymer on a fiber surface is so thin that any dislodgement of the fluorochemical may release the fluorochemical into the polymer film thereby allowing the fluorine to orient or project through the film with the required cure temperature of the polymer, reactivating the water surface contact angle so that the water repellent properties of the fluorochemical affect the finished product. However, regardless of physical or chemical explanation, the combination of polymer film and fluorochemical results in a fiber envelopment or cell or pore wall lining and the formation of encapsulated fibers and/or an internal layer of polymer in a web when this invention is practiced. After curing, the polymer is permanently fixed material.

By using the methods and apparatus of this invention, one can achieve a controlled placement of a polymer composition into a porous substrate or web to obtain a desired treated web.

A curable polymer such as used in the practice of this invention is applied under pressure using shear forces onto and into a web or substrate. The shear forces cause the curable silicone polymer to flow into the web. The extent of fiber envelopment and cell or pore wall lining is believed to be regulatable by controlling such factors as discussed previously, as well as the selection and applied amount of fluorochemical, if any, the curable polymer used, and the applied compressive and shear forces employed at a given temperature so that fiber envelopment is achieved while the interstices and/or open cells of the web are not completely filled with such polymer in the region of the internal layer, and the outer opposed surfaces of the web are substantially completely free of polymer coating or residue. After such a procedure, the curable polymer is then cured.

The curable polymer is applied onto the surface of the web. Then, the web, while tensioned, is passed over and against shearing means or through a compression zone, such as between rollers or against a shear knife. Thus, transversely applied shear force and compressive pressure is applied to the web. The combination of tension, shearing forces, and web speed is sufficient to cause the polymer to move into the web and out from the interstices or open cells around the web fibers, cells, or pores being enveloped. The result is that at least some of the interstices and/or open cells are unfilled in regions of the web outside of the region occupied by the internal coating or internal layer, and are preferably substantially free of polymer. Excess polymer is removed by the surface wiping action of the shearing means. The curable polymer enveloping the fibers is thereafter cured.

The desired penetration of, and distribution and placement of polymer in, a web is believed to be achieved by localized pressuring forces exerted on a web surface which are sufficiently high to cause the viscosity of a polymer composition to be locally reduced, thereby permitting such polymer to flow under such pressuring and to be continually placed within the web and to envelope its fibers or line the cell or pore walls thereof. To aid in this process, the web is preferably at least slightly distorted by tensioning or stretching, while being somewhat transversely compressed at the location of the controlled placement. This distortion is believed to facilitate the entrance of the polymer composition into the web. When the compression and tension are released, the polymer composition is believed to be squeezed or compressed within and through the interstitial spaces, or open cell spaces, of the treated web.

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If, for example, too much polymer is present in the finished product, then either or both the tension and shear force can be increased, and vice versa for too little polymer. If flow is not adequate upon the fibers, producing incomplete fiber envelopment, then the viscosity of the polymer composition can be reduced by increasing the resins and temperatures employed for the controlled placement thereof. Alternatively, if the viscosity is too low, then the pressure and/or temperature can be decreased. If the polymer composition is resistant to being positioned or placed in a desired location in a desired amount in a given web at various viscosities and/or pressures, then the level of fluorochemical pretreatment of the web can be increased, or decreased, as the case may be.

In one embodiment of this invention, polymer is forced into a web between two rollers. One such roller bears a polymer impregnant, typically and preferably distributed uniformly upon and over a circumferentially extending textured, or gravure surface. Such roller rotates (i) in the same direction as a facing roller and (ii) oppositely to the direction of movement of a continuously moving web traveling past the localized pressured area achieved between such roller and such moving web. The unidirectional rotation of the two rollers is believed to produce a distorting and stretching force or effect upon the web. This force is believed to promote penetration of the polymer into the web. This form of pressured application or coating can be termed "reverse roll coating" for convenience. Preferably, the reverse coating rollers have generally horizontal axis while the moving web moves generally horizontally. The web is further concurrently held longitudinally tensioned and distorted by being stretched against metering bars, bar knives, and the like which are urged against the web.

Such an initial pressured step is preferably followed by a series of further pressured web treatment steps believed to accomplish polymer reintroduction, polymer distribution, polymer scraping, and excess polymer removal and recovery. The collective result of such steps gradually produces a web wherein the polymer envelopes to a desired extent the fibers, or lines the cell or pore walls comprising the web and collects within a desired internal region or zone in the web thereby filling or plugging interstitial spaces, or open cells or pores, of the web in such region, but not filling the internal structure of the treated web with polymer beyond a desired extent. Particularly, and for example, in a fabric, a polymer composition may be made to substantially completely envelope the fibers or line the cells or pores thereof and fill the interstitial spaces thereof in such internal region.

In another embodiment of this invention, application of polymer to a web occurs from a reservoir. This reservoir of polymer is positioned tightly against the tensioned, moving web (or fabric). The linearly extending, preferably vertically upwardly moving, web (or fabric), constitutes a wall portion of the reservoir. Next, along the path of web travel, a bar or shear knife is pressed strongly and transversely against and laterally across the longitudinally tensioned web (or fabric). Further along the path of web movement, a shear blade or flexible scraper knife is also strongly and transversely forced laterally across and against the tensioned web. More than one shear knife, or more than one flexible compressive knife, can be successively positioned along the path of web movement. These blade means are believed to reintroduce the polymer into the web, to distribute the polymer, and to promote and complete the envelopment of fibers or lining of the cell or pore walls and fillage of interstices and open cells with polymer, and form an internal coating in a desired region in a web or encapsulate the fibers, or both. These

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scraper knives or shear blades are also believed to force the polymer further into the three-dimensional structure of the web. Also, these knives, particularly the scraper knives, wipe or scrape excess polymer off the surface of the web, and also extract polymer from within the web, thereby regulating the amount of polymer placed within the web.

The transversely applied shear forces applied across and against the web are sufficiently high to achieve temporarily and locally, a lowering of the viscosity of the preferably thixotropic viscous polymer. The lowered viscosity polymer is thus enabled to flow into, and upon, the internal three-dimensional structure of the web. Because the polymer composition that is being applied is subject to cure with heat or radiation and time, and because the pressured placement or shear thinning is believed to produce localized heat, the shearing conditions used prior to curing are preferably controlled to minimize premature curing. The properties of the polymer are preferably selected to be such that cure, or excessive cure, does not occur while the web is being treated with polymer during the shear thinning and controlled placement. The cure preferably occurs only after the web controlled placement procedure has been completed. Preferably, the cure temperature of the polymer composition is relatively high (preferably above about 250° F.) and the heat exposure time is such as is needed to obtain a desired solid resilient elastomeric polymer.

The viscosity of the polymer is preferably lowered by the high pressure (shear) forces exerted. However, such a pressure- and/or temperature-induced lowered viscosity should not go down too low, otherwise the polymer can flow substantially uncontrolled in the web in the manner of a low viscosity liquid that is saturated and impregnated into a web as is prior art web treatments. If the viscosity of the polymer composition is too low at the time of controlled placement then the web interstices or open cells can become excessively filled therewith, and the polymer is not, for example, reliably and controllably applied to achieve an envelopment of the structural elements (including fibers) of the web being treated together with internal coating formation.

Benzophenones, and particularly 2,4-dihydroxybenzophenone, are believed to be a particularly useful class of additives to the starting polymer composition, as hereinafter described.

As indicated above, the activity transpiring at a final step in the practice of this invention is generically referred to as curing. Conventional curing conditions known in the prior art for curing polymer compositions are generally suitable for use in the practice of this invention. Thus, temperatures in the range of about 250° F. to about 350° F. are used and times in the range of about 30 seconds to about 1 minute can be used, although longer and shorter curing times and temperatures may be used, if desired, when thermal curing is practiced. Radiation curing, as with an electron beam or ultraviolet light can also be used. However, using platinum catalysts to accelerate the cure while using lower temperatures and shorter cure times is preferable.

Since either filled, plugged, almost filled interstices, or open cells in the region of an internal layer remain transmissive of air in cured webs made by this invention, the webs are characteristically air permeable or breathable.

Sample webs or fabrics that are beneficially treated, fiber enveloped and internally coated in accordance with the invention include nylon, cotton, rayon and acrylic fabrics, as well as fabrics that are blends of fiber types. Sample nylon fabrics include lime ice, hot coral, raspberry pulp, and diva blue Tactel® (registered trademark of ICI Americas, Inc.) fabrics available from agent Arthur Kahn, Inc. Sample

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cotton fabrics include Intrepid® cotton cornsilk, sagebrush cotton, and light blue cotton fabrics available also from Arthur Kahn, Inc. Non-woven, monofilamentous, fabrics such as TYVEK® (registered trademark of E.I. duPont de Nemours Co., Inc.) and the like are also employable.

As indicated above, a web is preferably pretreated and impregnated with a fluorochemical prior to being treated with a polymer composition as taught herein. The fluorochemical impregnation is preferably accomplished by first saturating a web with a liquid composition which incorporates the fluorochemical, and then, thereafter, removing the excess liquid composition and residual carrier fluid by draining, compression, drying, or some combination thereof from the treated web.

It is now believed that any fluorochemical known in the art for use in web, particularly fabric treatment in order to achieve water repellency, soil repellency, grease repellency, or the like, can be used for purposes of practicing the present invention. It is believed that a typical fluorochemical of the type used for web treatment can be characterized as a compound having one or more highly fluorinated portions, each portion being a fluorinated radical or the like, that is (or are) functionally associated with at least one generally non-fluorinated organic portion. Such organic portion can be part of a polymer, part of a reactive monomer, a moiety with a reactable site adapted to react with a binder, or the like. Such a compound is typically applied to a fabric or other web as a suspension or solution in either aqueous or non-aqueous media. Such application may be conventionally carried out in combination with a non-fluorine or fluorine containing resin or binder material for the purpose of providing improved durability as regards such factors as laundering, dry cleaning, and the like.

Fluorochemicals are sometimes known in the art as durable water repellent (DWR) chemicals, although such materials are typically believed to be not particularly durable and to have a tendency to wash out from a fabric treated therewith. In contrast, fiber enveloped webs of this invention which have been pretreated with a fluorochemical display excellent durability and washability characteristics. Indeed, the combination of fluorochemical pretreatment and silicone polymer fiber envelopment such as provided by the present invention appears to provide synergistic property enhancement because the effects or properties obtained appear to be better than can be obtained by using either the fluorochemical or the silicone polymer alone for web treatment.

Exemplary water repellent fluorochemical compositions include the compositions sold under the name Milease® by ICI Americas Inc. with the type designations F-14N, F-34, F-31X, F-53. Those compositions with the "F" prefix indicate that they contain a fluorochemical as the principal active ingredient. More particularly, Milease® F-14 fluorochemical, for example, is said to contain approximately 18 percent perfluoromethyl acrylate copolymer, 10 percent ethylene glycol (CAS 107-21-1) and 7 percent acetone (CAS 67-64-1) dispersed and dissolved in 65 percent water. Milease® F-31X is said to be a dispersion of a combination of fluorinated resin, acetone, and water.

Still another suitable class of water repellent chemicals is the Phobotex® chemicals of Ciba/Geigy identified as Phobotex® FC104, FC461, FC731, FC208 and FC232 which are each believed to be suitable for use, typically in approximately a 5 percent concentration, in saturating a web for use in the invention. These and many other water repellent fluorochemicals are believed to be capable of creating a surface contact angle with water of greater than about 90 degrees when saturated into a web and to be suitable for use in the practice of this invention.

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Another group of useful water repellent fluorochromicals is the TEFLON®-based soil and stain repellents of E.I. duPont de Nemours & Co. Inc., 1007 Market Street, Wilmington, Del. 19898. Suitable TEFLON® types for use in the practice of this invention include TEFLON® G, NPA, SKE, UP, UPII, PPR, N, and MLV. The active water repellent chemical of each composition is believed to be a fluorochromical in polymeric form that is suitable for dispersion in water, particularly in combination with a cationic surfactant as a dispersant. These dispersions are dilutable in all proportions with water at room temperature. One preferred class of fluorochromical treating compositions useful in the practice of this invention comprises about 1 to about 10 weight percent, more preferably about 5 weight percent of one of the above indicated TEFLON®-type water repellent fluorochromicals in water.

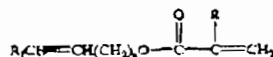
Another major group of suitable water repellent fluorochromical compositions useful in the practice of the invention is commercially available under the designation ZEPEL® rain and stain repellent chemicals of E.I. duPont de Nemours & Co. Inc., such as ZEPEL® water repellent chemicals types B, D, K, RN, RC, OR, HT, 6700 and 7040. Each is believed to be a fluorochromical in polymeric form that is dispersible in all proportions at room temperature. The dispersants ZEPEL® B, D, K, and RN are believed to be cationic, while the dispersant ZEPEL® RC is believed to be nonionic.

As an exemplary composition, ZEPEL® 6700 is said to be comprised of 15 to 20 percent perfluoroalkyl acrylic copolymer, 1 to 2 percent alkoxylated carboxylic acid, and 3 to 5 percent ethylene glycol. Exemplary characteristics of the composition include a boiling point of 100° C. at 760 mm Hg and a specific gravity of 1.08. The volatiles are approximately 80 percent by weight. The pH is 2 to 5. The odor is mild; the concentrate form is that of a semi-opaque liquid; and the concentrate color is straw white. The composition and characteristics of ZEPEL® 7040 repellent chemical are believed to be substantially identical to those of ZEPEL® 6700 except that the former composition additionally contains 7 to 8 percent acetone.

Another major group of water repellent fluorochromicals comprises the Scotchgard® water repellent chemicals of 3M Co., St. Paul, Minn. The Scotchgard® fluorochromicals are believed to be aqueously dispersed fluorochromicals in polymeric form. The compositions of two suitable Scotchgard® water repellent fluorochromicals are believed to be disclosed in U.S. Pat. Nos. 3,393,186 and 3,356,628, which patents are incorporated herein by reference. Thus, the Scotchgard® fluorochromical of U.S. Pat. No. 3,356,628 consists of copolymers of perfluoroacrylates and hydroxyalkyl acrylates. These copolymers are suitable for use as an oil and water repellent coating on a fibrous or porous surface. They have a carbon to carbon main chain and contain recurring monovalent perfluorocarbon groups having from 4 to 18 carbon atoms each and also having recurring hydroxyl radicals. From 20 to 70 percent of the weight of such copolymer is contributed by fluorine atoms in the perfluorocarbon groups and from 0.05 to 2 percent of the weight of the copolymer is contributed by the hydroxyl radicals. Such copolymer is said to have improved surface adhesion properties as compared to the homopolymer of a corresponding fluorocarbon monomer.

The Scotchgard® fluorochromical of U.S. Pat. No. 3,393,186 consists of perfluoroalkenylacrylates and polymers thereof. An exemplary fluorinated monomer has the formula:

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Wherein R_1 is a fluorocarbon group having from 3 to 18 carbon atoms, R is hydrogen or methyl, and n is 0-16. Such a water repellent fluorochromical composition is supplied and saturated into the substrate web as a readily pourable aqueous dispersion.

U.S. Pat. No. 4,426,476 discloses a fluorochromical textile treating composition containing a water-insoluble fluorolipophilic radical, an aliphatic chlorine-containing ester and a water insoluble, fluorolipophilic radical containing polymer.

U.S. Pat. No. 3,896,251 discloses a fluorochromical textile treating composition containing a fluorolipophilic radical containing linear vinyl polymer having 10 to 60 weight percent fluorine and a solvent soluble carbodiimide preferably comprising fluorolipophilic groups. A table in this patent lists a plurality of prior art fluorolipophilic radical containing polymers useful for the treatment of fabrics and the prior art patents where such polymers are taught.

U.S. Pat. No. 3,328,661 discloses textile treating solutions of a copolymer of an ethylenically unsaturated fluorocarbon monomer and a ethylenically unsaturated epoxy group containing monomer.

U.S. Pat. No. 3,398,182 discloses fluorocarbon compounds useful for fabric treatment that contain a highly fluorinated oleophobic and hydrophobic terminal portion and a different nonfluorinated oleophilic portion linked together by a urethane radical.

Water repellent fluorochromical compositions are preferably utilized to saturate a starting untreated porous web substrate so that such composition and its constituents wet substantially completely and substantially uniformly all portions of the web. Such a saturation can be accomplished by various well known techniques, such as dipping the web into a bath of the composition, or padding the composition onto and into the web, or the like. Padding is the presently preferred method of fluorochromical application.

After application of the fluorochromical composition to the web, the water (or liquid carrier) and other volatile components of the composition are removed by conventional techniques to provide a treated web that contains the impregnated fluorochromical throughout the web substrate.

In a preferred procedure of fluorochromical controlled placement, a web is substantially completely saturated with an aqueous dispersion of a fluorochromical. Thereafter, the resulting impregnated web is compressed to remove excess portions of said dispersion. Finally, the web is heated to evaporate the carrier liquid. If the fluorochromical is curable, then the heating also accomplishes curing. After the fluorochromical treatment, the fluorochromical is found only on or in the web structural elements or fibers and is substantially completely absent from the web interstices.

The fluorochromical concentration in the treating composition is such as to permit a treated fluorochromical containing web, after volatiles of the treating composition are removed, to exhibit a contact angle with water applied to an outer web surface which is greater than about 90°. More preferably, the contact angle provided is greater than about 130°.

The web weight add-on provided by the fluorochromical after removal of volatiles is usually relatively minor. However, the weight add on can vary with such factors as the nature of web treated, the type of polymer composition utilized in the next step of the process, the temperature at

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which the composition is applied, the ultimate use contemplated for a web, and the like.

Typical weight add-ons of fluorochemicals are in the range of about 1 to about 10 percent of the original weight of the web. More preferably, such weight add-ons are about 2 to about 4 weight percent of the weight of the starting fabric.

Durability of a web that has been treated with a fluorochemical and durability of a web that is subsequently treated with a polymer can sometimes be improved by the conventional process of "sintering". The exact physical and chemical processes that occur during sintering are unknown. The so-called sintering temperature utilized is a function of the fluorochemical composition utilized and such temperature is frequently recommended by fluorochemical manufacturers. Typically, sintering is carried out at a temperature of about 130 to about 160° C. for a period of time of about 2 to about 5 minutes. Acid catalysts can be added to give improved durability to laundering and dry cleaning solvents.

The fluorochemical is believed to provide more than water or other repellent properties to the resulting treated web, particularly since the curable polymer is often itself a water repellent. Rather, and without wishing to be bound by theory, it is believed that the fluorochemical in a treated web provides relative lubricity for the treated fibers during the pressure application of the curable polymer. The polymer is applied under pressures which can be relatively high, and the polymer is itself relatively viscous, as is discussed herein. In order for the curable polymer to coat and envelop web fibers, but not fill web interstitial voids, the fibers of the web may move over and against each other to a limited extent, thereby to permit entry of the polymer into and around the fibers. It is thought that the fluorochemical deposits may facilitate such fiber motion and facilitate envelopment during the pressure application and subsequent shearing processing.

Alternatively, the fluorochemical may inhibit deposition of the polymer at the positions of the fluorochemical deposits which somehow ultimately tends to cause thin enveloping layers of polymer to form on fibers.

The precise physics and chemistry of the interaction between the fluorochemical and the polymer is not understood. A simple experiment demonstrates movement of the liquid polymer as influenced by the presence of the fluorochemical.

A piece of fabric, for example the Red Kap Milliken poplin polyester cotton blend fabric, is cut into swatches. One swatch is treated with an adjuvant, for example a three percent solution of the durable water-repellent chemical Milease® F-31X. The treated swatch and an untreated swatch are each positioned at a 45° angle to plumb. A measured amount, for example one-half ounce, of a viscous polymer composition, for example the Mobay® 2530A/H silicone composition, is dropped onto the inclined surface of each swatch. The distance in centimeters that the composition flows downwards upon the surface of the swatch is measured over time, typically for 30 minutes.

A graphical plot of the flow of the silicone composition respectively upon the untreated and treated swatches over time can be prepared, such as shown in FIG. 1. At the expiration of 30 minutes the viscous composition has typically traveled a distance of about 9.8 centimeters upon the treated swatch, or a rate of about 0.24 centimeters per minute. At the expiration of the same 30 minutes, the viscous composition has typically traveled a lesser distance of about 7.1 centimeters upon the untreated swatch, or a rate of about 0.24 centimeters per minute. Qualitatively commensurate results are obtainable with other DWR fluorochemical adjuvants that facilitate the viscous flow of polymer composi-

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tions in accordance with the invention. Indeed, if desired, the simple flow rate test can be used to qualify an adjuvant compound for its employment within the method of the invention. The fluorochemical pretreated web generally increases the surface contact angle of the polymer while reducing the amount of saturation of the polymer into the fibers themselves.

The fluorochemical treated web is thereafter treated under pressure with a predetermined amount of a curable polymer composition to form a web whose fibers are preferably substantially completely enveloped with such curable polymer and whose outer surfaces and interstices are preferably substantially completely free of the curable polymer. The polymer is thereafter cured by heat, radiation, or the like. Even room temperature curing can be used. A polymer impregnated, fluorochemical pretreated web can be conveniently stored before being subjected to curing conditions depending upon the storage or shelf life of the treating silicone polymer composition.

A curable polymer composition utilized in the practice of this invention preferably has a viscosity that is sufficient to achieve an internal coating of the web. Generally, the viscosity is greater than about 1000 centipoise and less than about 2,000,000 centipoise at a shear rate of 10 reciprocal seconds. It is presently most preferred that such composition have a viscosity in the range of about 5,000 to about 1,000,000 centipoise at 25° C. Such a composition is believed to contain less than about 1% by weight of volatile material.

The polymer is believed to be typically polymeric and to be commonly a mixture of co-curable polymers, oligomers, and/or monomers. A catalyst is usually also present, and, for the presently preferred silicone polymer compositions discussed hereinafter, is platinum or a platinum compound, such as a platinum salt.

A preferred class of liquid curable silicone polymer compositions comprises a curable mixture of the following components:

- (A) at least one organo-hydrosilane polymer (including copolymers);
- (B) at least one vinyl substituted polysiloxane (including copolymers);
- (C) a platinum or platinum containing catalyst; and
- (D) (optionally) fillers and additives.

Typical silicone hydrides (component A) are polymethylhydrosiloxanes which are dimethyl siloxane copolymers. Typical vinyl terminated siloxanes are vinyl dimethyl terminated or vinyl substituted polydimethylsiloxanes. Typical catalyst systems include solutions or complexes of chloroplatinic acid in alcohols, ethers, divinylsiloxanes, and cyclic vinyl siloxanes.

The polymethylhydrosiloxanes (component A) are used in the form of their dimethyl copolymers because their reactivity is more controllable than that of the homopolymers and because they result in tougher polymers with a lower cross-link density. Although the reaction with vinyl functional silicones (component B) does reportedly take place in 1:1 stoichiometry, the minimum ratio of hydride (component A) to vinyl (component B) in commercial products is reportedly about 2:1 and may be as high as 6:1. While the hydrosilation reaction of polymethylhydrosilane is used in both so called RTV (room temperature vulcanizable) and LTV (low temperature vulcanizable) systems, and while both such systems are believed to be useful in the practice of the present invention, systems which undergo curing at elevated temperature are presently preferred.

Elastomers produced from such a curing reaction are known to demonstrate toughness, tensile strength, and dimensional stability.